U.S. DEPARTMENT OF COMMERCE
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PB80-116833

Treatability of Carcinogenic and Other Hazardous Organic Compounds

IIT Research Inst, Chicago, IL

Prepared for

Municipal Environmental Research Lab, Cincinnati, OH

Aug 79

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-79-097
August 1979

Research and Development

PB80-116833

EPA

Treatability of Carcinogenic and Other Hazardous Organic Compounds

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-79-097		PB 80 116833

4. TITLE AND SUBTITLE	5. REPORT DATE
TREATABILITY OF CARCINOGENIC AND OTHER HAZARDOUS ORGANIC COMPOUNDS	August 1979 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Edward G. Fochtman and Walter Eisenberg	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
IIT Research Institute 10 West 35th Street Chicago, Illinois 60616	1BC611, SOS #5,Task AE/02
	11. CONTRACT/GRANT NO.
	Contract No. CI-68-03-2559
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory-Cinti,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati,Ohio 45268	Final (6/17/77- 6/17/78)
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Richard A. Dobbs (513/684-7649)

16. ABSTRACT

This research program was conducted to determine the capability of biological and physical-chemical treatment processes to remove chemical carcinogens and other hazardous organic compounds from water and wastewater. Treatment processes investigated included biological degradation, activated carbon adsorption and oxidation with ozone. Compounds studied were naphthalene, 1,1-diphenylhydrazine, β-naphthylamine, 4,4'-methylene-bis (2-chloroaniline), and dimethylnitrosamine. All compounds were amenable to biological treatment in continuous flow reactors. Ozone and activated carbon provided effective treatment for all except dimethylnitrosamine.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sewage Treatment*, Chemical Removal (Sewage Treatment)*, Activated Carbon Treatment	Physical-Chemical Treatment Biological Treatment	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	72
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	A04 - A01

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE 1979-657-146/5469

EPA-600/2-79-097
August 1979

TREATABILITY OF CARCINOGENIC AND OTHER HAZARDOUS ORGANIC COMPOUNDS

by

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Contract No. CI-68-03-2559

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Many chemical carcinogens have been identified in effluents from municipal wastewater treatment plants and in drinking water supplies. This report presents the results of a study of the treatability of five chemical carcinogens found in wastewater. Three treatment systems, biodegradation, carbon adsorption, and ozone oxidation were studied. The treatment procedures indicate significant differences in the treatability of the compounds.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Three methods of wastewater treatment, carbon adsorption, biodegradation, and ozone oxidation were evaluated as potential treatment processes for wastewater containing five different chemical carcinogens at levels of 1 mg/ℓ or less. The laboratory scale treatment techniques and analytical procedures gave results that indicated that

naphthalene	can be treated by all three techniques but reacts with ozone very slowly
1,1-diphenylhydrazine	can be treated by all three processes
β-naphthylamine	can be treated by all three processes
4,4'-methylene-bis (2-chloroaniline)	can be treated by all three processes
dimethylnitrosamine	resists ozone oxidation, is not adsorbed by carbon, is biodegraded in continuous biological reactors.

This report was submitted in fulfillment of Contract No. CI-68-03-2559 by IIT Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1977 to June 1978.

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ABBREVIATIONS AND SYMBOLS

BNA -- β-naphthylamine
BZ -- benzidine
DCB -- 3,3^{1}-dichlorobenzidine
DMNA -- dimethylnitrosamine
DPH -- 1,1-diphenylhydrazine
GAC -- granular activated carbon
HPLC -- high performance liquid chromatography
KD -- Kuderna-Danish
MOCA -- 4,4^{1}-methylene-bis (2-chloroaniline)
NAP -- naphthalene

ACKNOWLEDGMENTS

IITRI gratefully acknowledges the cooperation of the National Cancer Institute, which provided the chemical carcinogens from the NCI repository and the advice and assistance of R. A. Dobbs, EPA Program Officer, who provided many valuable suggestions on equipment set-up, analytical procedures, and data presentation.

Victor Ivanuski, H. J. O'Neill, Christine Rachwalski, Peter Kroll, and Raleigh Farlow, members of the IITRI staff, contributed to the program.

SECTION 1

INTRODUCTION

A 1976 survey indicated that many toxic and carcinogenic chemicals were present in treated municipal wastewater. Some of these compounds are known to persist in the environment and could very well find their way into drinking water supplies, Public Law 92-500 and the Toxic Substance Control Act are aimed at regulating the amount of these toxic substances discharged to the environment. Public Law 93-523, the Safe Drinking Water Act, placed increased emphasis on the need to treat wastewater to insure removal of toxic chemicals to the lowest possible level.

The Environmental Protection Agency has been directed to develop treatment processes to remove toxic organic compounds from water and wastewater. Many physical, chemical, and biological processes are already available to reduce the concentration of these toxic chemicals in aqueous solutions to very low levels. Hundreds of organic compounds have been identified in drinking water supplies and treatment techniques for meeting the Interim Primary Drinking Water Regulations are being proposed and developed.

The work at IITRI was directed toward the development of treatment techniques to prevent the release of organic chemical carcinogens in municipal wastewater to the environment.

The chemicals of primary concern were:

naphthalene
diphenylhydrazine
β-naphthylamine
4,4-methylene-bis (2-choroaniline)
dimethylnitrosamine
benzidine
3,3-dichlorobenzidine
benzanthracene
acrylonitrile
chloromethyl methyl ether
ethyleneimine

The first five compounds of this list were used in three types of treatment; the next two were studied in less detail, exploratory work was conducted on an additional two compounds. The five were subjected to three treatment processes described in this report. Three treatment methods compatible with

processes currently being considered for municipal wastewater were investigated:

Biodegradation - the treatment method of choice for most municipal wastewaters

Carbon Adsorption - under very active study and evaluation for the tertiary treatment of municipal wastewater

Ozone Oxidation - /disinfection - proposed for tertiary treatment of municipal wastewater and plants are under construction.

While the ideal study technique would utilize municipal wastewater from many sites as the source water for this study such a program would require a very large effort to develop definitive results and probably would not be cost-effective. For this study a mineralized distilled water contaminated with the compound of interest was used in order to develop the first level of information. Later studies may be conducted using wastewater from selected municipal facilities.

SECTION 2

CONCLUSIONS

The treatability of five chemical carcinogens in wastewater by biodegradation, carbon adsorption, and ozone oxidation was determined. Biodegradation was tested in both static and continuous reactors; two commercially available granular activated carbons were used for determining adsorption; and ozone oxidation was studied in a 12-liter reactor using 1 percent ozone in oxygen.

naphthalene (NAP)

- NAP was readily degraded in the static biological reactor.
- NAP was fairly easily adsorbed; 29 mg of granular activated carbon, (GAC) per liter reduced the concentration from 1 ppm to 0.1 ppm.
- NAP and its decomposition products reacted rapidly with ozone; half-life of the NAP was dependent upon relative amounts of the reactants.
- NAP was readily stripped from the aqueous solution.

1,1-diphenylhydrazine (DPH)

- DPH was readily degraded in the static biological reactors.
- DPH was easily adsorbed; 18 mg of GAC per liter reduced the concentration from 1 ppm to 0.1 ppm.
- DPH was quickly destroyed in the ozone reactor forming several reaction products.

β-naphthylamine (BNA)

- BNA was only partially degraded in the static biological reactor but was completely destroyed in the continuous biological reactor.
- BNA was fairly easily adsorbed; 37 mg of GAC per liter reduced the concentration from 1.0 ppm to 0.1 ppm.
- BNA did not readily strip from the ozone reactor but did react with the ozone to give a half-life of 1.6 min.

4,4-methylene-bis (2-chloroaniline) (MOCA)

- MOCA was not degraded in the static biological reactor but was degraded in the continuous biological reactor.
- MOCA was fairly easily adsorbed; 33 mg of GAC per liter reduced the concentration from 1.0 ppm to 0.1 ppm.
- MOCA was not stripped from the ozone reactor; its half-life with ozone was 3 min.

dimethylnitrosamine (DMNA)

- DMNA was partially degraded in the static biological reactors; concentration was reduced from 50-70 percent. It was destroyed in the continuous biological reactors; 2 ppm concentrations were reduced to <0.1 ppm.
- DMNA was not effectively adsorbed by GAC.
- DMNA did not react with ozone nor was it effectively stripped from the solution.

One objective of the program was to develop treatability tests which could be used for study of additional compounds. The results for these five compounds have covered a range of results and indicate broad applicability. The compounds studied have included:

(1) Compounds treatable in static biological reactors (NAP, DPH)

(2) Compounds not treatable in static biological reactors but treatable in continuous biological reactors (DMNA, BNA, MOCA)

(3) Compounds that can be adsorbed by GAC (NAP, DPH, BNA, MOCA)

(4) Compounds that not effectively be adsorbed by GAC, (DMNA)

(5) Compounds that are stripped from a gas-liquid reactor (NAP)

(6) Compounds that cannot be stripped from an ozone reactor but readily react with ozone (BNA, MOCA)

(7) Compounds that are neither stripped nor reacted in the ozone reactor.

It was determined that no one treatment process removed all compounds and that all compounds studied could be treated by at least one of the processes.

SECTION 3

RECOMMENDATIONS

It is recommended that these treatability studies be continued and expanded. Additional chemical carcinogens found in municipal wastewater should be studied. The carbon adsorption and ozone oxidation studies should be expanded to include either an actual municipal wastewater or a simulated municipal wastewater.

SECTION 4

MATERIALS AND METHODS

SELECTION OF COMPOUNDS TO BE STUDIED

All of the compounds studied, except for naphthalene, were selected from the list of 14 chemical carcinogens published by NIOSH. The compounds selected were chosen on the basis of their stability in water, water solubility, and the availability of analytical techniques. Solubility data for concentrations of interest were very limited.

The investigation of a number of compounds was halted during the program. These compounds included benz(a)anthracene, 2,7-dichlorodibenzo-p-dioxin, 1,2-diphenylhydrazine, benzidine and 3,3-dichlorobenzidine. Benz(a)anthracene and 2,7-dichlorodibenzo-p-dioxin were eliminated from consideration because their solubilities were below the concentration range selected in the experimental protocol (less than 0.3 ppm).

During the carbon adsorption studies it was discovered that 1,2-dipheynlhydrazine was unstable and readily converted to azobenzene with time. 1,1-diphenylhydrazine of acceptable purity was substituted for this compound.

The analysis of benzidine proved difficult at the ppm level and below. The analytical procedure consisted of the following steps: solvent extraction with methylene chloride, drying and concentration with a K-D evaporation, and analysis by high performance liquid chromatography with ultraviolet absorption detection. The recovery of benzidine from mineralized water spiked at the one ppm level could not be reproduced and varied from 33.0 to 79.9 percent. The method was scrutinized to determine the source of variability in the analysis. In the drying and concentration steps of the procedure, benzidine recovery was quantitative. In a single experiment it was further shown that only 55 percent of the benzidine in a sample was recovered by extraction. Attempts to find the remaining benzidine failed. It was shown that there was no benzidine remaining in the water sample after the original extraction, and further there was not benzidine adsorbed onto the surface of the glass separatory funnel. It can only be concluded that the missing benzidine was lost in some way. The procedure was abandoned at this point since it did not appear that these difficulties could be easily overcome.

BIOLOGICAL DEGRADATION

A simple static screening test for the assessment of the biodegradability of organic compounds, reported by Bunch and Chambers,[1] formed the basis of the static tests performed during this study. Bunch and Chambers conducted the

the test at room temperature using a 200 ml nutrient solution based on yeast extract in a flask without a shaker. We increased the scale of the test and used 2,000 ml of solution in 1 gal glass containers in order to obtain a sample large enough to give reliable analysis.

Bunch and Chambers seeded the nutrient/organic solution with sewage and allowed the bacteria to act on the nutrient and organic for 7 days. After analyzing the organic they used a 10 percent aliquot of the 7-day mixture to seed a fresh nutrient/organic mixture. This procedure was repeated until 28 test-days had been completed.

Baird, Carmonan, and Jenkins[2] used conventional Warburg techniques to assess the toxic effect of selected aromatic amines on organisms found in typical activated sludges. Their dosage levels exceeded manyfold the solubility levels of some compounds. Gas chromatographic or colormetric analysis was used. They were able to measure depletion of the organic as well as its toxic effect on the sewage organisms.

While the Warburg technique permits rapid screening of the toxicity of compounds it does not confirm the degradation. The limited sample size does not permit analysis of very low concentrations by current HPLC techniques.

Static reactors are convenient to use and require little equipment, however, continuous biological reactors better simulate the treatment that municipal wastewater normally receives. Laboratory reactors can be made to simulate this continuous biological system. Such units can be operated steady state and give reliable results if they are carefully designed and operated. We used a continuous reactor with an aeration chamber of about 300 ml. Sludge separated in the side arm while treated water overflowed at the top of the sidearm. Sterilized nutrient solution containing the organic was pumped to the reactor. The flow through the reactor generally exceeded 1 liter per day, providing a sample which was adequate for most analyses.

In a study of the biodegradation of benzidine, Tabak and Barth[3] used 5.7 liter aerobic suspended growth reactors and the supernatant from settled domestic wastewater for a 7-week test period. The feed was doped with as high as 32 ppm of benzidine, which was degraded to 10-12 ppm.

Carbon Adsorption

The adsorption of organics from aqueous solutions has been used in a wide variety of applications and is currently being evaluated for the purification of municipal wastewater. Early results have been promising and, if the final evaluation of carbon adsorption is favorable, there is a real possibility that the process will be utilized by many municipalities.

V. L. Snoeyink[4] studied the adsorption of humic substances in combination with trace amounts of chlorophenols and polynuclear hydrocarbons at various pH levels and developed corresponding mathematical descriptions.

The Freundlich adsorption isotherm is generally used to describe the adsorption equilibrium and can be expressed as:

$$\frac{X}{M} = KC_f^{1/n}$$

where X is $C_o - C_f$

C_o is Amount of organic in the untreated solution

C_f is Amount of organic in the treated solution

M is Weight of adsorbent (carbon)

K is Empirical constant

n is Empirical constant

K is the X intercept of the plot of the isotherm at $C_f = 1$ and 1/n is the slope of the line on logarithmic paper.

The equation can be rearranged to permit easy calculation of the carbon dosage required to reduce an initial concentration to a specified residual concentration. If $(C_o - C_f)$ is substituted for X the equation becomes:

$$\frac{C_o - C_f}{M} = KC_f^{1/n}$$

This equation is linear when M, the carbon dose, is plotted against C_o, the initial concentration, on ordinary coordinate paper.

The isotherm data can be used to calculate countercurrent dosages of carbon. This technique treats a solution with fresh carbon, and removes the carbon by filtration. The solution is then treated with a second batch of fresh carbon, which is also recovered by filtration and used to treat a batch of the more concentrated feed material.

Although the extensive carbon adsorption literature has reports on the adsorption of pesticides,[5,6] fatty acids,[7] amines,[8,9] aromatics,[8] and chlorinated hydrocarbons, there is very limited published data on the adsorption of carcinogenic compounds at low, 1 mg/ℓ, and lower concentrations. The work reported here dealt with chemicals identified as carcinogens.

Ozone Oxidation

Ozone has long been used to treat drinking water in Europe. Only two U.S. cities, Philadelphia, Pennsylvania and Whiting, Indiana were treating drinking water with ozone at the time of the International Conference on Ozone in Chicago, Illinois in 1959. A Second International Conference in Washington, D.C. in 1973[9] appears to have generated more widespread interest in ozone for drinking water and wastewater treatment. Since 1973 several additional symposia have been held much research and pilot plant data has been generated, additional treatment plants have been activated, many new plants are being designed, and nine plants are under construction. The current largest U.S.

plant at Springfield, Missouri, uses 3600 lbs ozone per day to treat 30 MGD of municipal wastewater.

In chemical kinetics studies it is usually found that the rate of reaction is proportional to the concentrations of the two substances reacting:

$$\frac{dC}{dt} = -kC[O_3] \qquad (1)$$

where C is concentration of pollutant, mg/ℓ

$[O_3]$ is concentration of ozone, mg/ℓ

t is time, min

k is rate constant, ℓ/mg-min

If ozone is present in large excess, then $[O_3]$ will not vary with [C]. Then Equation 1 integrates to

$$\ln \frac{C_1}{C_2} = -k[O_3]\Delta t \qquad (2)$$

where subscripts 1 and 2 refer to times t_1 and t_2,

$\Delta t = t_2 - t_1$

Equation 2 implies that for each interval of time, Δt, the concentration decreases by a constant ratio. If the ratio is 1/2, then Δt is the half-life. Thus either half-life or rate constant k is a suitable measure of treatability by ozone. In these studies we have used half-life of the compound under a specific set of reactor conditions as a measure of ozone oxidation treatability.

SECTION 5

EXPERIMENTAL PROCEDURES

GENERAL PROCEDURES

The laboratory procedures used during these studies were based upon published reports of the treatment of water containing low concentrations of organic chemicals and upon in-house experience. The use of carcinogenic chemicals imposed a number of restrictions and precautions concerning the amounts of materials, concentrations, laboratory manipulations, protective clothing, ventilation, and waste disposal.

All standard solutions of carcinogens were prepared and handled by staff who are under medical surveillance in a facility especially designed for chemical carcinogens. These staff members also doped the aqueous solutions to be treated. Analytical staff and the principal laboratory investigator were also under medical surveillance.

Wastes from the laboratory work were incinerated in equipment which services the laboratories using chemical carcinogens.

Since many of the materials studied had limited solubility, in the range of 2 mg/ℓ, water with very low organic chemical content was prepared by reverse osmosis, deionization, and filtration through a membrane filter. With less than 0.01 mg/ℓ organic carbon, this water caused negligible analytical background.

The composition of water likely to be encountered in field situations was simulated with mineralized water. Table 1 describes the composition of the mineralized water. (Preparation procedures appear in Appendix A).

TABLE 1. COMPOSITION OF MINERALIZED WATER

Ion	Conc., mg/ℓ	Ion	Conc., mg/ℓ
Na^+	92	$PO_4^{\equiv}$	10
K^+	12.6	$SO_4^{=}$	100
Ca^{++}	100	Cl^-	177
Mg^{++}	25.3	$alkalinity^+$	200

TREATABILITY STUDIES

Treatability is the removal or decomposition of a compound in water. Treatability experiments measure the amount of the compound remaining in the water after various durations of treatment. Important variables are the initial concentration of the compound, the duration of treatment, and perhaps other conditions such as temperature and pH. During this program the experimental procedures for the three basic methods of treatment were established. Use of these procedures will permit the comparison of the ease of treatment of various compounds by each treatment procedure.

Biological Degradation

Two types of biological degradation tests, a static test and a continuous test, were conducted. Those compounds which were not degraded in the static test were tested in the continuous mode.

The static test, patterned after the procedure of Bunch and Chambers, seeded a 2-liter carcinogen-doped nutrient solution with supernatant liquid from the mixed liquor return line of the activated sludge wastewater treatment plant (southwest) of the Metropolitan Sanitary District of Greater Chicago.

The seeded nutrient solution was placed in 1-gallon clear glass bottles and the desired concentration of carcinogen, usually 2.0 mg/ℓ, was added as an alcohol solution. The bottles were placed on the bench top and occasionally agitated during the next 7 days. A 1-liter sample was then taken for analysis, and another 200 ml was withdrawn to seed a fresh nutrient solution. The mixture was again doped with the desired amount of carcinogen and the test continued for another 7 days. Visible differences in the apparent viscosity, color, and turbidity of the solutions were observed.

The continuous tests simulated the activated sludge process on a very small laboratory scale. Glass reactors (See Figure 1) with a capacity of approximately 300 ml in the aerated chamber were used. This gave a hold-up time of 6 hours at a flow of 1.2 liters per day.

The continuous reactors were seeded at start-up with the same material as used for the static tests. Feed consisted of the same nutrient-carcinogen doped solution as used with the static test, except that the nutrient solution, which had to be prepared daily, was heat-sterilized before adding the carcinogen. A composite 24-hour sample was taken each seventh day for analysis.

The preparation procedure for the nutrient solution used in both the static and continuous tests is given in the appendix.

Carbon Adsorption

A series of eight 1-liter glass-stoppered reagent bottles were used for each carbon adsorption isotherm determination. Automatic pipettes were used to charge clean and well-rinsed bottles with a known amount of an aqueous suspension of activated carbon of known concentration. The bottles were filled with the doped water to the bottom of the stopper to avoid ullage over

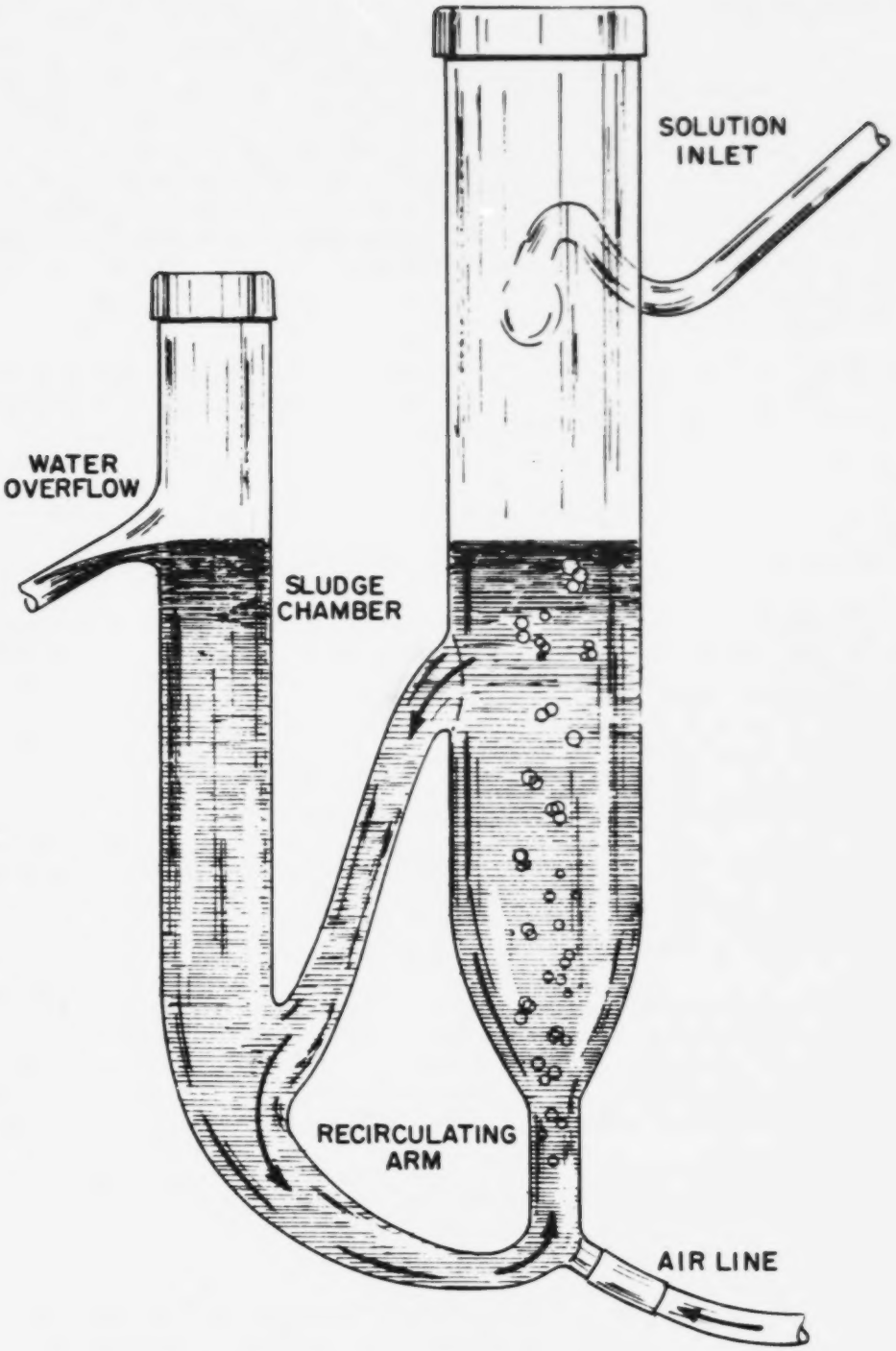


Figure 1. Drawing of continuous biological reactor.

the solution. The suspensions were agitated with magnetic stirrers for at least 2 hours before removing a sample for analysis.

Six carbon-adsorption samples were obtained from the eight bottles. One bottle served as a control and did not receive any carbon nor was it filtered. A second bottle did not receive carbon but was filtered. These two samples served as an analytical control for assessing the role of filtration in removing the organic from the water. Initial studies indicated that glass fiber filters adsorbed only very small amounts of the organic. The filtered sample also indicated whether or not the organic was completely dissolved or remained as finely divided undissolved particles.

Two granular activated carbons, Filtrasorb 400 and Darco KB, were used to assess adsorption characteristics of the organic. The granular carbons were ball-milled for 24 hours, then sieved. The process was repeated until 90-95 percent of the material passed the 200 mesh screen. The minus 200 mesh material was composited and used for the entire program.

Samples were analyzed by u.v. absorption or by extraction, concentration, and HPLC, with a u.v. detector or capillary gas chromatograph with a nitrogen detector.

Ozone Oxidation

The ozone treatability studies assessed the technical feasibility of reducing organic carcinogens to acceptable concentration by oxidation with ozone.

The laboratory equipment and procedures selected for the ozone treatability studies were derived from many technical and mechanical/physical considerations as listed below.

Technical Factors--

1. The reactor must provide for good mass transfer of the ozone from the gas to the liquid.

2. It must be possible to measure or make a reasonable estimate of the ozone concentration in the water.

3. Concentrations must permit measurement of reaction times.

4. Stripping of the contaminant must be determined.

5. Compensation for ozone autodecomposition may be necessary.

6. Detection of any by-products remaining in the water is desirable.

Operational Factors--

1. The reactor must be sufficiently large to permit withdrawal of approximately five samples, as large as 1 liter each, during a run and continue to function effectively.

2. The reactor must be as small as practical to minimize the amount of carcinogen that must be handled.

3. The reactor must be capable of easy decontamination.

4. Ozone concentration in the gas must be representative of that either currently used or proposed by engineers designing plant installations.

Initially, ozone concentration was measured in the gas and in the water by the standard methods. Later, ozone concentration in the gas was measured with a Dasibi Environmental Corp. ozone monitor and in the water with a Delta Scientific Co. ozone monitor. The equilibrium ozone concentration in water was found to be close to that reported in the literature. The Welsbach literature gives:

$$\frac{\text{mg/}\ell\ O_3 \text{ in water}}{\text{mg/}\ell\ O_3 \text{ in } O_2} = 0.20 \text{ (at 30°C)}$$

The concentration of ozone in the water under treatment is a function of the concentration in the gas, the supply rate, temperature, autodecomposition, and the reaction with dissolved organics. The autodecomposition rate is highly dependent upon pH.

Since the organic, especially volatile, compounds, may be stripped from the solution by the gas, it is important that the gas flow rate be representative of the flow rate that may be encountered in the field.

Gloyna and Eckenfelder[11] give an example of diffused aeration where 3,400 cfm is used in an 81,000 cu ft tank, or 0.042 liters of air per liter of water. This value is based upon a biological aeration system and is lower than the gas flow rate used by investigators studying the effect of ozone.

Lambert[12] relates that five different research teams investigating the effect of temperature on the ozonation of simulated mobile hospital wastewater reported widely varying results. He attributes part of the variance to the widely different ozone reactors, which ranged from round-bottom flasks, to commercially available fermentors, to pilot-scale, multi-stage continuously-stirred tank reactors.

See[13] used a flow rate of 23.6 liters per minute in a 14-liter stirred reactor or 1.7 liters of gas per minute per liter of water in his study of the treatment of a mobile hospital wastewater.

Pileg[14] used a small, 1-liter reactor, and a gas flow of 40 liters per hour or 0.67 liters per minute of gas per liter of reactor volume in a study of two different types of municipal wastewater.

Shambaugh and Melnyk[15] used a 1-liter stirred reactor equipped with a sparger and a gas flow of 0.6 liters per minute. At 1 wt% ozone in the gas, the water reached a concentration of about 0.5 mg O_3/liter after 90 seconds. This is approximately the equilibrium concentration at pH = 9. A study of the relative rates of mass transfer and ozone decomposition at various pH levels

showed that a pH change from 8.0 to 9.0 decreased the steady state ozone concentration in their reactor by a factor of three.

Rosen[16] cites operating and planned ozone dosages as:

Location	Ozone Dose
Woodlands, TX	8 mg/ℓ
Indiantown, FL	10
Estes Park, CO	6
Mahoning Co., OH	6
Springfield, MO	10
Pensacola, FL	6

Armstrong[17] states that an ozone dose of 3.25 mg/ℓ was required for disinfection of secondary treatment plant effluent.

Naimie[18] noted the relationship between ozone demand and suspended solids for a pure oxygen activated sludge system as:

	Water Analysis, mg/ℓ		Ozone Demand mg/ℓ
	TSS	COD	
Filtered Effluent	0	30	1.0 - 2.5
Gravity Filtered	6	30	1.5 - 4
Unfiltered	15-30	30	3.5 - 8.5

Since most municipal secondary treatment effluents contain 20 mg/ℓ Total Suspended Solids, an ozone demand of 8 mg/ℓ may be realistic.

Selection of the gas flow rate for the laboratory studies is important since the flow rate affects the rate of stripping of the organic from the water. Dilling[19] gives the evaporation as:

$$H = \frac{C_{air}}{C_{water}} = \frac{16.04\ PM}{TS}$$

where H is Henry's law constant

C_{air} is equilibrium concentration in air

C_{water} is equilibrium concentration in water

P is vapor pressure of pure solute in mmHg

M is gram molecular wt of solute

T is temperature, °K

S is solubility of solute in water mg/ℓ.

This equation gives an indication of the stripping of the organic; however, the limited solubility and vapor pressure data restricts the use.

On the basis of this brief review and our in-house experience it was decided to set up the ozone treatability reactor as follows:

Reactor volume:	12 liters
Reactor diameter:	8½ in.
Reactor height:	14 in.
Agitator:	4-blade turbine
Sparger:	coarse glass frit
Gas flow:	2.4 ℓpm
Ozone concentration:	1 wt%

Ozone dose rate:

$$\frac{2.4 \text{ liters gas/min}}{12 \text{ liters water}} \times \frac{1.4 \text{ gm}}{\text{liter}} \times .01 = 2.8 \text{ mg/ℓ/min}$$

pH: 7.5

Temperature: ambient, 25°C.

ANALYTICAL PROCEDURES

Wherever possible, analytical procedures used in the program were based upon published EPA procedures. Analytical techniques involved HPLC, u.v. absorption, and capillary gas chromatography.

High Performance Liquid Chromatography (HPLC) - Ultraviolet Adsorption

The volume of the sample was measured in a graduated cylinder, and the sample was transferred to a 2-liter separatory funnel. The graduated cylinder was washed with the extracting solvent (distilled-in-glass methylene chloride) which was then transferred to the separatory funnel.

Neutral Extraction--

The sample was serially extracted with three portions of methylene chloride. In the case of a liter sample, 400 X 150 X 150 ml portions were used. Each sample was extracted for 1 minute by the clock. In cases where the concentration was known to be high (>2 ppm) a proportionally small amount of sample was used.

Basic Extraction--

The pH of the sample was adjusted to 11 or greater with 6N NaOH using multi-range pH paper. The sample was extracted as described in the neutral extraction.

Acid Extraction--

The pH of the sample was adjusted to 2 or less with 6N HCℓ using multi-range pH paper. It was extracted as described in the neutral extraction.

Extract Drying--

The combined solvent extracts were dried and filtered by passing these through a short column of anhydrous sodium sulfate which had been prewashed in the column with methylene chloride. After drying the extract. the sodium sulfate was rinsed with the extracting solvent which was added to the extract.

Extract Concentration--

The solvent extract was concentrated to ~20 ml in a Kuderna-Danish (KD) apparatus fitted with a 3-ball macro-Snyder column and a 10-ml calibrated receiver tube. Then 5 ml of distilled-in-glass methanol were added and the extracts were evaporated to 5 ml. When the KD apparatus had cooled to room temperature, the receiver was removed and a micro-Snyder column was attached. The extract was carefully evaporated to a volume suitable for analysis usually 3 ml, and the internal standard, phenanthrene, was added.

Samples not analyzed immediately were stored in amber vials with Teflon inserts at refrigerator temperatures. No loss of methylene chloride was observed during storage if the vials were tightly sealed.

High Performance Liquid Chromatographic Analysis--

The samples were analyzed on a Waters Model 244 ALC/GPC liquid chromatograph equipped with a Model 660 Solvent Programmer for gradient elution and a Schoeffel HS870 ultraviolet absorption detector. Elution of the samples on a 30 cm x 4 mm Bondapak C_{18} column was achieved using a methanol water gradient going from 60 percent to 100 percent methanol in 20 minutes.

These elution conditions were used for β-naphthylamine, 1,1-diphenylhydrazine, and 4,4'-methylene-bis(2-chloroaniline). In the case of naphthalene, the samples were eluted isocratically at a solvent composition of 80 percent methanol:20 percent water. The solvent flow rate was 2 ml per minute in all cases. Table 2 provides the absorption wavelength used for each compound, and the limit of detection for each.

High Resolution Gas Chromatography - Flame Ionization Detection

This procedure was used for the analysis of benzidine and 3,3-dichlorobenzidine and is a modification of one reported by M. Bowman and C. Nony.[18]

The volume of the sample was measured in a graduated cylinder and the sample was transferred to a 500 ml liter separatory funnel. The graduated cylinder was washed with the extracting solvent (distilled-in-glass benzene) and this was transferred to the separatory funnel.

Basic Extraction--

The pH of the solution was adjusted to 11 or greater with 6N NaOH using multi-range pH paper. The sample, usually 250 ml, was extracted with three portions of benzene 40 x 20 x 20 ml.

TABLE 2. ABSORPTION WAVELENGTH AND LIMITS OF DETECTION USING HPLC

Compound	Absorption Wavelength (nm)	Detection Limit
Naphthalene	280	100 ng
β-Naphthalene	280	80 ng
4,4'-Methylene-bis(2-chloroaniline)	280	60 ng
1,1-Diphenylhydrazine	280	100 ng
Benzidine	265	60 ng

Extract Drying--

The combined solvent extracts were dried and filtered by passing these through a short column of anhydrous sodium sulfate. The sodium sulfate was prewashed in the column with benzene. After drying the sodium sulfate was rinsed with the extracting solvent and this was added to the extract.

Extract Concentration--

The solvent extract was concentrated to 2 ml in a Kuderna-Danish apparatus fitted with a 3-ball macro-Snyder column, and a 4 ml calibrated receiver tube. The concentration was performed under a slight vacuum, obtained using a water aspirator.

Derivatization--

A pentafluoropropronic anhydride (PFP) derivative was prepared for the aromatic amines, benzidine and 3,3-dichlorobenzidine. In this procedure, one drop of triethylamine was added to the sample (~2 ml) in a 20 ml vial, followed by the addition of .5 ml of PFP reagent. The tube was immediately sealed, shaken, and heated in a 50°C water bath for 20 minutes. The reaction was terminated by adding 5 ml of phosphate buffer, pH - 6.0. The tube was shaken for 1 minute, and after the phases were separated, the aqueous layer was discarded. The extraction was repeated with an additional 5 ml of buffer. The benzene layer was separated and the internal standard, 2,6-dimethylnaphthalene, was added. The sample was then analyzed by high resolution gas chromatography.

A Hewlett Packard Model 5840A gas chromatograph was used for the analyses. The samples were chromatographed on a 25 meter OV-17 glass capillary column. The chromatographic conditions are given below.

initial temperature - 150°C held for 6 min after injection

program - 150°C to 225°C at a rate of 4° per minute

flow - 7 cm^3/sec

split - 19/1

attenuation - 16 x 10^{-12} amps/mv

The limit of detection was 50 nanograms for each compound.

Spectrophotometric Analysis

Concentration of aromatic compounds were measured in the carbon absorption experiments through spectrophotometric analysis. Ultraviolet absorption was measured by Cary 14 spectrophotometer with 1 and 10-cm cells. All dilutions of the compounds were freshly prepared in mineralized water. (The absorption wavelengths utilized are given in Table 3). Readings were corrected for solvent blanks, and absorptions were plotted vs. concentrations for the compounds to produce a standard curve. (Data for the calibration curves are given in Table 4).

QUALITY CONTROL

Reagent Control

Each time a sample or group of samples was to be analyzed, a standard solution containing the internal standard and the compound under analysis were analyzed to maintain instrument control. Duplicate analyses were found to agree to within $\pm$ 2%. The records of these analyses were kept with the sample and blank records. A blank is an experiment that undergoes all analytical procedures, except that no compound other than the internal standard is present.

Data Control

All experimental data was recorded on laboratory data sheets and transcribed into bound IITRI logbooks.

Accuracy and Precision

The accuracy and precision of the high performance liquid chromatography is given in Table 5. Duplicate analyses were performed on water samples spiked with individual compounds at the level of 0.5 ppm.

TABLE 3. ABSORPTION WAVELENGTH AND DETECTION LIMIT FOR UV ABSORPTION

Compound	Wavelength (nm)	Detection Limit (ppm)
Benzidine	281	0.17
β-Naphthylamine	285	0.08
4,4'-Methylene-bis(2-chloroaniline)	240	0.30
Naphthalene	276	0.20
1,1-Diphenylhydrazine	230	0.05

TABLE 4. STANDARD CURVES FOR ANALYSIS BY UV ABSORPTION

Compound	m	b	r	
Benzidine	7.306	-0.0887	0.99999	1.0 cm cell λ = 281.5 nm
Naphthalene	3.9330	-0.0820	0.9998	10 cm cell λ = 276 nm
4,4-Methylene bis(2-chloro-aniline)	2.0606	-0.0225	0.999	10 cm cell λ = 240 nm
1,1-Diphenyl-hydrazine	16.487	+0.067	0.998	1.0 cm cell λ = 230 nm
β-Naphthylamine	28.075	+0.091	0.999	1.0 cm cell λ = 285 nm

X = optical density (O.D.).

Y = mX + b (equation of the line obtained by linear regression analysis of the calibration)

Y = compound concentration (mg/ℓ).

m = slope of the line.

b = intercept.

r = correlation coefficient.

λ = wavelength.

TABLE 5. ACCURACY AND PRECISION DATA

Compound	Percent Recovery
1,1-Diphenylhydrazine	83.3 $\pm$ 4.4
4,4'-Methylene-bis(2-chloroaniline)	84.0 $\pm$ 3.2
β-Naphythylamine	99.7 $\pm$ 2.4
Naphthalene	95.4 $\pm$ 1.2

SECTION 6

RESULTS AND DISCUSSION

The three procedures used to treat dilute aqueous solutions of these carcinogens resulted in a range of removal. Some compounds were almost completely removed by one treatment procedure, whereas other treatment procedures were ineffective. The range of treatability of each compound for each process is discussed in the following sections.

BIOLOGICAL DEGRADATION

Two types of biological degradation were used: a static and a continuous system. Those compounds which were not degraded during static tests were treated in a continuous biological reactor.

Static Biological Degradation Tests

All of the compounds under study were screened by the static biological test. In these test biological seed from an activated sludge plant were supplied with the nutrient solution which had been doped with approximately 2 ppm of the carcinogen. The growth was allowed to continue for 7 days, a sample removed, and a fresh doped nutrient solution seeded with 10 percent of the solution from the previous week. Results of these tests are presented in Table 6.

Naphthalene was readily degraded during the static biological test. After a weeks acclimatization, the naphthalene was reduced from 2 ppm to nondetectable during the 7-day test.

1,1-Diphenylhydrazine was also reduced from 2 ppm to nondetectable levels during the 7-day biological test.

β-Naphthylamine was reduced by about 40 percent (2.15 to 1.26 mg/ℓ) after a 10-week acclimatization period.

4,4'-Methylene-bis(2-chloroaniline) was not effectively biologically decomposed during the static tests.

Dimethylnitrosamine was partially decomposed in the static biological tests.

TABLE 6. STATIC BIOLOGICAL DEGRADATION TESTS (All values in mg/ℓ)

	Naphthalene	Dimethyl-nitrosamine	1,1-Diphenyl-hydrazine	β-Naphthyl-amine	4,4'-Methylene-bis(2-chloro-aniline)
Original Culture					
Doped	1.97	1.82	2.02	2.07	2.12
7-Day	0.12	0.52	Lost	1.04	1.90
1st Sub-Culture					
Doped	1.76	1.88	2.24	1.77	2.16
7-Day	N.D.	0.52	1.20	1.67	2.42
2nd Sub-Culture					
Doped	2.02	1.88	2.15	1.73	2.08
7-Day	N.D.	1.0	1.03	1.78	2.31
3rd Sub-Culture					
Doped	2.12	2.33	2.48	1.92	1.81
7-Day	0.06	1.0	N.D.	1.91	1.76
4th Sub-Culture					
Doped	1.98	1.98	2.05	2.25	2.11
7-Day	N.D.	0.9	N.D.	2.00	2.09
5th Sub-Culture					
Doped	1.95	2.30	2.32	1.96	2.10
7-Day	N.D.	1.40	N.D.	1.30	1.95
6th Sub-Culture					
Doped	1.96	--	2.17	2.04	2.01
7-Day	N.D.	--	N.D.	1.66	1.89

(continued)

TABLE 6 (continued)

	Naphthalene	Dimethyl-nitrosamine	1,1-Diphenyl-hydrazine	β-Naphthyl-amine	4,4'-Methylene-bis(2-chloro-aniline)
7th Sub-Culture					
Doped	--	--	--	1.74	--
7-Day	--	--	--	1.07	--
8th Sub-Culture					
Doped	--	--	--	2.42	--
7-Day	--	--	--	1.77	--
9th Sub-Culture					
Doped	--	--	--	1.93	--
7-Day	--	--	--	1.53	--
10th Sub-Culture					
Doped	--	--	--	2.15	--
7-Day	--	--	--	1.21	--
11th Sub-Culture					
Doped	--	--	--	2.15	--
7-Day	--	--	--	1.26	--
				stop	

N.D. = nondetectable.

Continuous Biological Reactor Tests

Three compounds were tested using the continuous biological reactors:

- 4,4-methylene-bis (2-chloroaniline)
- dimethylnitrosamine
- β-naphthylamine

Fresh nutrient solution was prepared and doped every day. Table 7 records the level of contaminant in the nutrient solution given on the day before the effluent sample was collected. Thus, the nutrient solution containing 1.78 mg/ℓ dimethylnitrosamine was started through the system on the 6th day of the test and the effluent was collected for the next 24 hours and analyzed (0.42 mg/ℓ).

TABLE 7. CONTINUOUS BIOLOGICAL DEGRADATION TESTS (All values mg/ℓ)

Day of Test	Dimethyl-nitrosamine	β-Naphthyl-amine	4,4'-Methylene-bis (2-chloroaniline)
6 Doped	1.78	2.11	2.02
7 Effluent	0.42	0.28	0.09
13 Doped	1.86	2.03	2.00
14 Effluent	0.27	0.25	0.09
20 Doped	2.29	1.79	2.19
21 Effluent	0.08	.32	N.D.
27 Doped	2.29	1.80	2.33
28 Effluent	0.1	--	0.13
34 Doped	1.93	1.93	1.95
35 Effluent	<0.01	.09	0.05
41 Doped	2.24	2.20	1.79
42 Effluent	<0.1	N.D.	N.D.

Dimethylnitrosamine was readily decomposed in the continuous biological reactor. Concentrations of 2.29 mg/ℓ were reduced to between 0.09 and 0.01 mg/ℓ. The side arm and recirculation leg of the reactor clogged with large flocs and some floc remained in the aerated chamber.

4,4'-Methylene-bis (2-chloroaniline) was degraded from 2.02 to 0.09 mg/ℓ in the biological reactor. Small white flocs formed and circulated freely throughout the system.

β-Naphthylamine was readily decomposed in the continuous biological reactor; it was reduced from 2.11 to 0.22 mg/ℓ at the end of the first week and during extended operation the biomass appeared to adapt to the BNA until at 6 weeks it was reduced from 2.20 mg/ℓ to non-detectable (<0.1 ppm).

CARBON ADSORPTION

All carbon adsorption studies were conducted to determine the isotherms using two commercially available granulated activated carbons, Darco KB and Filtrasorb 400. Table 8 presents the results for each compound studied, giving the Freundlich parameters, correlation coefficients, and adsorption capacity of each carbon for each compound. Isotherms and actual data are given in the appendix.

The adsorption capacity of the carbons varied about twofold for those compounds that were adsorbed. The compounds absorbed had very limited solubility, while the DMNA was readily soluble and was not adsorbed.

OZONE OXIDATION

Most of the compounds studied were oxidized by ozone; for some, products of the oxidation were observed during the analysis.

For these treatability studies the half-life of the compound was used to characterize the reactivity or treatability. Correction was made for the stripping of the compound from solution by the oxygen. Some compounds reacted with the oxygen-saturated water without application of ozone. The compounds studied and the method of test indicated a wide spread in the stripping and ozone reactivity of the compounds. Compounds such as MOCA and DMNA were very stable to oxygen stripping. DMNA was stable to ozone oxidation while MOCA was readily degraded. Data for each of these compounds are presented in the appendix and summarized in Table 9.

Ozone solubility in water in equilibrium with 1 percent ozone in oxygen was about 3 to 4 mg/ℓ at the conditions of the test. This is not a large excess of ozone and at times the rate of disappearance of the compound of interest may have been limited by ozone concentration. Naphthalene can illustrate this point. One would expect that several different reactions are involved in the oxidation of naphthalene to carbon dioxide and water. First the primary reaction involving naphthalene and the formation of a secondary compound. This secondary compound (and subsequent degradation products) compete for the available ozone. If the secondary products have a reaction rate with ozone much greater than the NAP/ozone rate the ozone in the system is depleted until the secondary product is consumed.

The above considerations make it necessary to compare the ozone oxidation characteristics of compounds under identical experimental conditions.

TABLE 8. FREUNDLICH PARAMETERS AND CAPACITY OF GAC

Compounds	Mol. wt	pH	Freundlich Parameters K	Freundlich Parameters 1/n	Correl. Coef.	Adsorption Capacity at 1 ppm mg/gm Carbon	mg Carbon per Liter to Reduce from 1.0 mg/ℓ to 0.1 mg/ℓ
Naphthalene	128						
Darco		7.5	58	0.276	0.982	58	28
Filtrasorb		7.5	176	0.524	0.993	176	17
1,1-Diphenyl-hydrazine	184						
Darco		7.5	92	0.257	0.918	92	19
Filtrasorb		7.5	135	0.158	0.751	135	10
β-Naphthylamine	143						
Darco		7.5	67	0.395	0.819	67	36
Filtrasorb		7.5	150	0.302	0.939	150	12
4,4'-Methylene-bis (2-chloroaniline)	264						
Darco		7.5	93	0.554	0.957	93	35
Filtrasorb		7.5	188	0.637	0.895	188	21
Dimethylnitrosamine	74						
Darco		7.5	1.4×10^{-6}	8.15	0.715	1.4×10^{-6}	--
Filtrasorb		7.5	6.8×10^{-5}	6.57	0.617	6.8×10^{-5}	--

TABLE 9. SUMMARY OF OZONE OXIDATION STUDY RESULTS

Compound	Stripping half-life, min.	Ozone reaction half-life, min.
Naphthalene	(1)	(2)
1,1-Diphenylhydrazine	0.5	0.4
β-Naphthylamine	<45	1.6
4,4'-Methylene-bis (2-chloroaniline)	(3)	(5)
Dimethylnitrosamine	(4)	(5)

(1) Readily stripped; half-life time dependent upon gas flow and initial concentration.

(2) Fast reaction; half-life time dependent upon initial concentration and ozone feed rate.

(3) Not stripped; <1% in 40 min.

(4) Not stripped; <1% in 130 min.

(5) No reaction; <1% in 130 min.

The HPLC results for naphthalene are given in Figure 2. The compound plus an internal standard is indicated. Two minutes after the start of the reaction a second compound appeared and increased in concentration through the 70-minute reaction period. No attempt was made to identify this compound. During this time the ozone concentration in the solution was less than the saturation value, thus indicating the reaction was mass-transfer limited.

When β-naphthylamine was reacted with ozone it was very rapidly degraded. The analysis of the samples taken during the first 4.5 minutes of the reaction are shown in Figure 3.

The ozonation of 1,1-diphenylhydrazine resulted in several by-products as indicated in Figure 4.

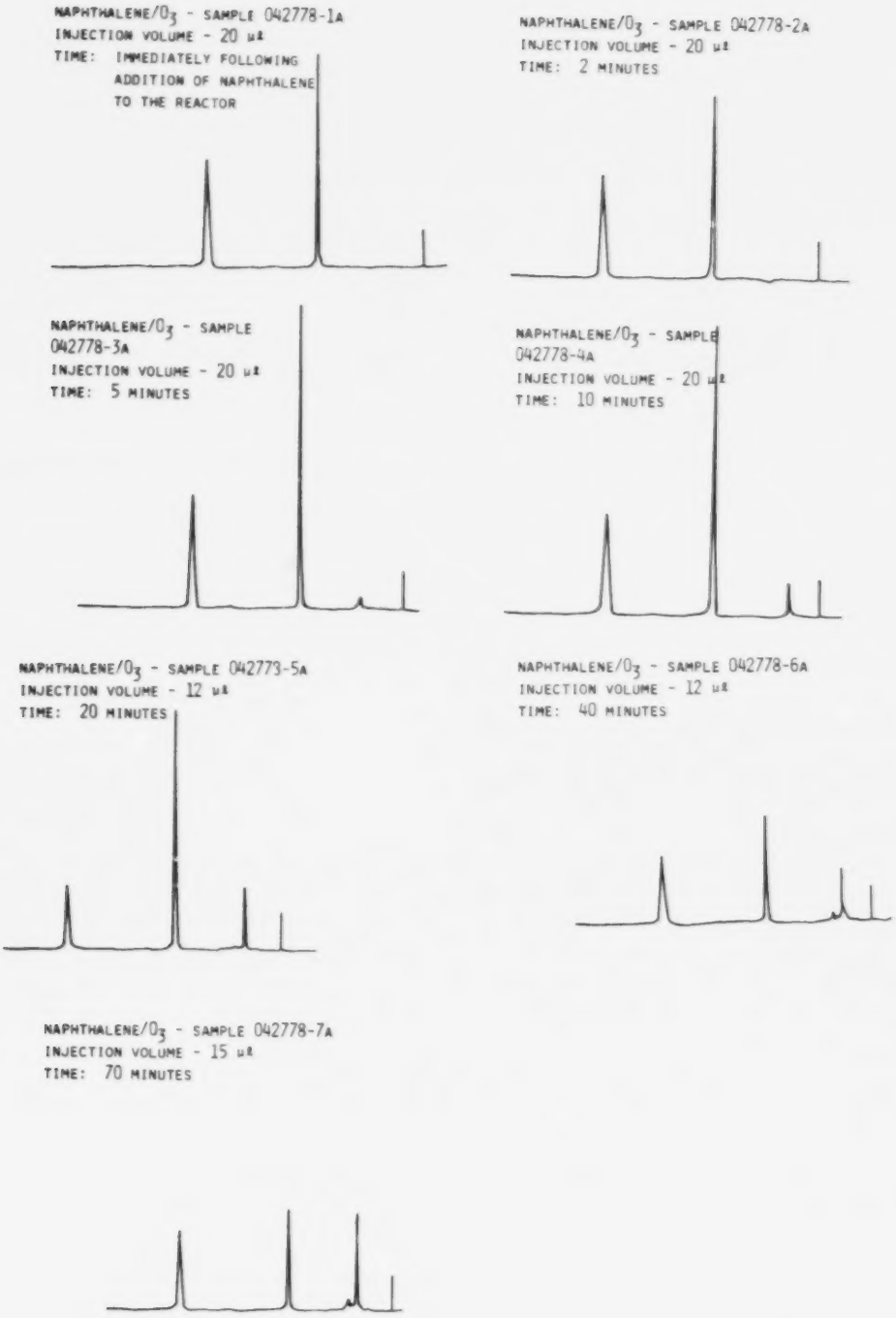
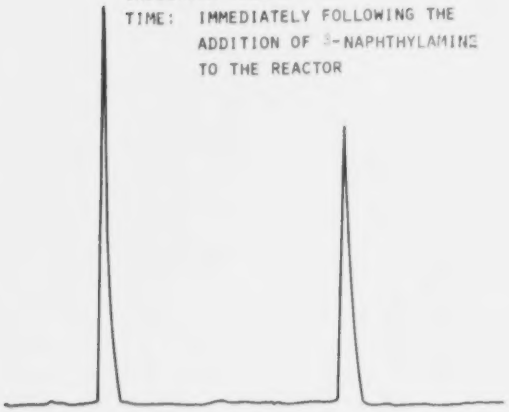
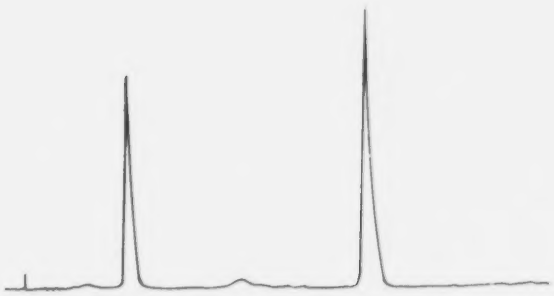

NAPHTHALENE/O_3 - SAMPLE 042778-1A
INJECTION VOLUME - 20 µL
TIME: IMMEDIATELY FOLLOWING ADDITION OF NAPHTHALENE TO THE REACTOR
NAPHTHALENE/O_3 - SAMPLE 042778-2A
INJECTION VOLUME - 20 µL
TIME: 2 MINUTES
NAPHTHALENE/O_3 - SAMPLE 042778-3A
INJECTION VOLUME - 20 µL
TIME: 5 MINUTES
NAPHTHALENE/O_3 - SAMPLE 042778-4A
INJECTION VOLUME - 20 µL
TIME: 10 MINUTES
NAPHTHALENE/O_3 - SAMPLE 042773-5A
INJECTION VOLUME - 12 µL
TIME: 20 MINUTES
NAPHTHALENE/O_3 - SAMPLE 042778-6A
INJECTION VOLUME - 12 µL
TIME: 40 MINUTES
NAPHTHALENE/O_3 - SAMPLE 042778-7A
INJECTION VOLUME - 15 µL
TIME: 70 MINUTES

FIGURE 2. HPLC ANALYSIS OF OZONATED NAPHTHALENE 5 MICRON ZORBOX ODS IN A 4.6 MM x 25.0 CM COLUMN; SOLVENT: METHANOL: WATER (80:20, V:V); ISOCRATIC ELUTION FLOW RATE: 1 ML/MIN; 25°C; 1500 PSI; DETECTION: UV AT 280 MM; SENSITIVITY 1.0 AUFS

β-NAPHTHYLAMINE/O_3 - SAMPLE 041878-1A
INJECTION VOLUME - 20 µℓ
TIME: IMMEDIATELY FOLLOWING THE ADDITION OF β-NAPHTHYLAMINE TO THE REACTOR



β-NAPHTHYLAMINE/O_3 - SAMPLE 041878-2A
INJECTION VOLUME - 20 µℓ
TIME: 1.5 MINUTES



β-NAPHTHYLAMINE/O_3 - SAMPLE 041878-3A
INJECTION VOLUME - 20 µℓ
TIME: 4.5 MINUTES

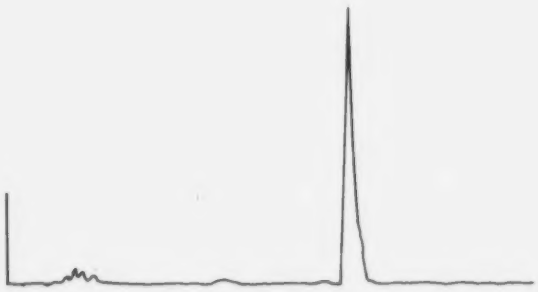


FIGURE 3. HPLC ANALYSIS OF OZONATED β-NAPHTHYLAMINE 10 MICRON µ BONDPAK C18 COLUMN IN A 4.0 MM X 30.0 CM COLUMN; SOLVENT: METHANOL: WATER (60:40, v:v) PLUS 1% ACETIC ACID; LINEAR GRADIENT ELUTION, 60% METHANOL TO 100% METHANOL IN 20 MINUTES; FLOW RATE 2 M^1/MIN; 25 C; 1500 PSI; DETECTION: UV AT 280 NM; SENSITIVITY 1.0 AUFS

1,1-DIPHENYLHYDRAZINE/O_3 - SAMPLE 041378-1A
INJECTION VOLUME - 15 µL
SENSITIVITY - 1.0 AUFS
TIME: IMMEDIATELY FOLLOWING THE ADDITION OF 1,1 - DIPHENYLHYDRAZINE TO THE REACTOR

1,1-DIPHENYLHYDRAZINE/O_3 - SAMPLE 041378-2A
INJECTION VOLUME - 15 µL
SENSITIVITY - 1.0 AUFS
TIME: 2 MINUTES

1,1-DIPHENYLHDRAZINE/O_3 - SAMPLE 041378-3A
INJECTION VOLUME 25 µL
SENSITIVITY - 0.1 AUFS
TIME: 6 MINUTES

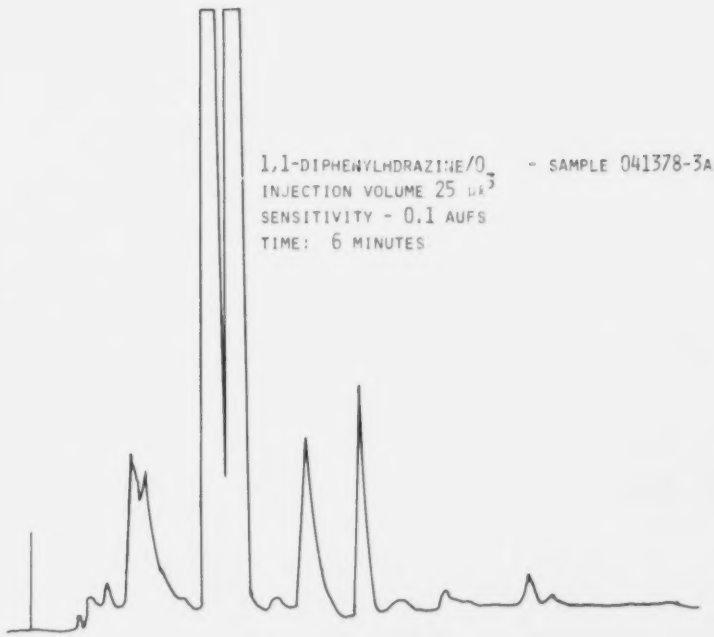


FIGURE 4. HPLC ANALYSIS OF OZONATED 1,1 - DIPHENYLHYDRAZINE 10 MICRON µ BONDAPAK C18 IN A 4.0 MM X 30.0 CM COLUMN; SOLVENT: METHANOL: WATER (60:40, V:V) PLUS 1% ACETIC ACID; LINEAR GRADIENT ELUTION, 60% TO 100% METHANOL IN 20 MINUTES; FLOW RATE, 2 ML/MIN; 25°C; 1500 PSI; DETECTION: UV AT 280 NM

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APPENDIX A

OZONE REACTION DATA

TABLE A-1. STRIPPING AND OZONATION OF NAPHTHALENE (25°C)

Time (min)	Oxygen Flow ℓ/min	Oxygen Wt. % O_3	Ozone in Water mg/ℓ	pH	Naphthalene mg/ℓ
			STRIPPING		
0	2.4	0	0	---	6.48
2	2.4	0	0	---	5.91
5	2.4	0	0	---	5.93
10	2.4	0	0	---	--
20	2.4	0	0	---	2.54
40	2.4	0	0	---	3.49
			OZONATION		
0	2.4	0.8	0.0	8.2	7.36
2	2.4	0.8	0.7	8.0	6.54
5	2.4	0.90	.85	7.9	5.97
10	2.4	.98	.30	8.2	5.24
20	2.4	.97	.15	---	3.48
40	2.4	.97	.12	8.2	1.46
70	2.4	.98	.05	---	1.16

TABLE A-2. STRIPPING AND OZONATION OF 1,1 DIPHENYLHYDRAZINE

(25°C)

Time (min)	Gas Flow ℓ/min	Wt. % Ozone	1,1-Diphenyl-hydrazine, mg/ℓ
		STRIPPING	
0	2.4	0	9.98
1	2.4	0	2.88
7	2.4	0	0.86
12	2.4	0	N.D.[1]
22	2.4	0	N.D.[2]
		OZONATION	
0	2.4	1.00	9.9
2	2.4	1.01	0.35
6	2.4	1.01	N.D.[3]
12	2.4	1.00	N.D.[3]
30	2.4	1.01	N.D.

N.D. = Nondetectable.

[1]Secondary products, 13 peaks on hplc.

[2]15 peaks on hplc.

[3]20 peaks on hplc.

TABLE A-3. STRIPPING AND OZONATION OF β-NAPHTHYLAMINE

(24°C)

Time (min)	Gas Flow ℓ/min	Wt. % Ozone	pH	β-Naphthylamine mg/ℓ
		STRIPPING		
0	2.4	0	-	11.6
5	2.4	0	-	11.6
15	2.4	0	-	11.2
25	2.4	0	-	12.2
45	2.4	0	-	11.3
		OZONATION		
0	2.4	1.00	-	11.0
1.5	2.4	1.02	8.0	5.94
4.5	2.4	1.03	8.1	.01[1]
10	2.4	1.03	6.8	.08[2]
20	2.4	1.01	6.4	.06[2]
40	2.4	1.01	6.6	.04[2]

[1]4 peaks on hplc.

[2]Decomposition products caused some interference.

TABLE A-4. STRIPPING AND OZONATION OF 4,4'-METHYLENE-BIS(2-CHLOROANILINE)

Time (min)	Gas Flow ℓ/min	Ozone Wt. %	pH	MOCA mg/ℓ
		STRIPPING		
0	2.4	0	---	1.59
2	2.4	0	---	1.82
5	2.4	0	---	1.81
10	2.4	0	---	1.75
20	2.4	0	---	1.69
40	2.4	0	---	1.77
		OZONATION		
0	2.4	1.10	7.0	1.52
2	2.4	1.08	7.5	1.01
5	2.4	1.07	8.2	N.D.*
10	2.4	1.07	7.0	N.D.
20	2.4	1.06	7	N.D.
40	2.4	1.00	7	N.D.
70	2.4	1.00	7	N.D.
100	2.4	0.99	7	N.D.

*N.D. = Nondetectable.

TABLE A-5. STRIPPING AND OZONATION OF N-DIMETHYLNITROSAMINE

Time (min)	Ozone Wt. %, Gas	pH	Ozone ppm in H_2O	N-DMNA (mg/ℓ)
0	0	---	0.05	10
2	1.06	---	3.9	7
4	1.05	8.8	4.3	6
8	1.07	---	4.3	6
15	1.00	9.0	3.3	6
30	1.00	8.9	2.5	5
60	1.00	8.3	2.0	5
90	1.00	8.2	2.0	5
120	1.00	8.2	2.1	5
0	0	7.3	.05	35*
2	1.00	6.3	.05	29
5	1.02	4.5	.5	39
11	1.02	0	4.6	39
20	1.01	0	3.8	33
40	1.00	0	3.4	30
70	1.01	0	4.1	31
100	1.01	4.7	4.2	29
130	1.00	4.5	3.7	30

*Run made with distilled water in place of mineralized water.

CARBON ADSORPTION DATA

COMPOUND: Naphthalene/Darco

STRUCTURE:

FORMULA: $C_{10}H_8$ **MOL. WT.** 128.19

FREUNDLICH PARAMETERS	pH		
	7.5		
K	58.3		
1/n	0.276		
Corr. Coef. r	0.982		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	110		
1.0	58		
0.1	30.9		

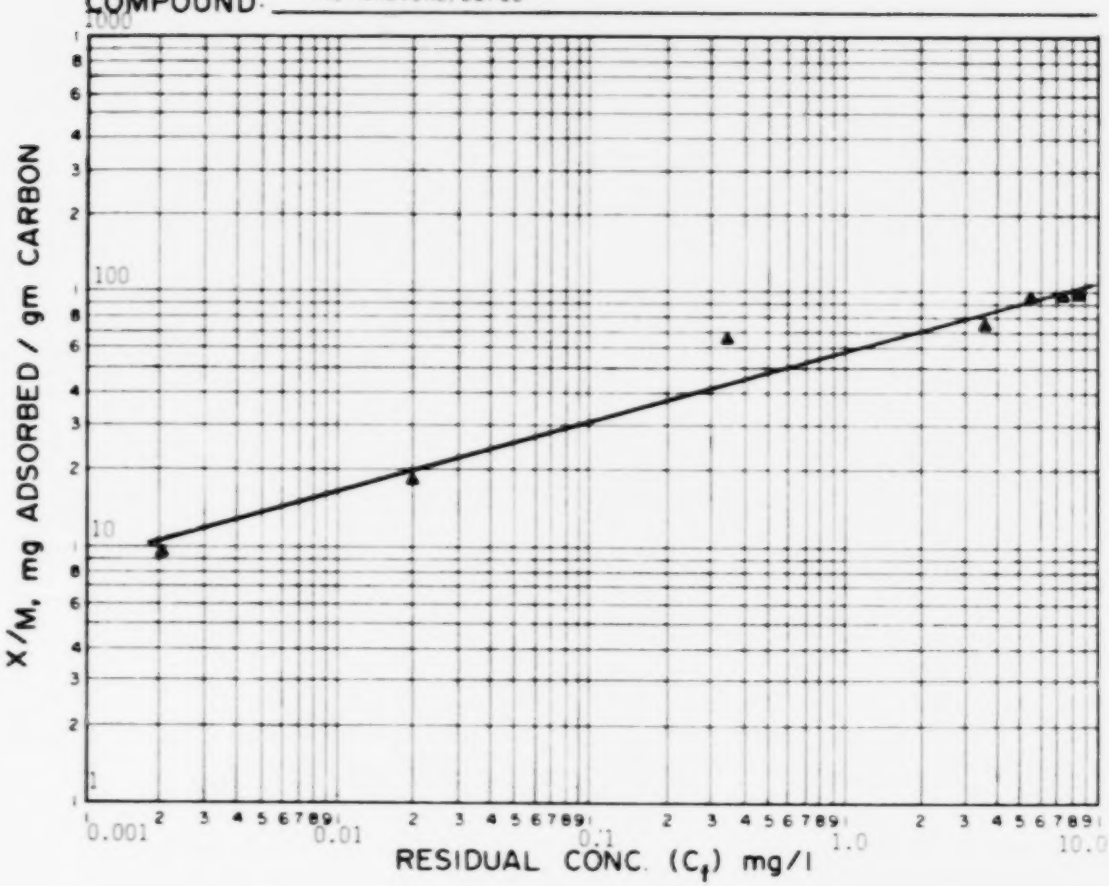
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

Co, mg/l	C_f, mg/l 1.0	0.1	0.01	0.001
10	154	312	611	1154
1.0	--	28	61	12
0.1	--	--	6	1
0.01	--	--	--	--

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

COMPOUND: Naphthalene/Darco



	pH = 7.5			pH =			pH = 7.5		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	9.30				Carbon Dose /l				
4.04	9.30	--	--			0	0.96	--	
10.23	8.30	1.00	97			9.9	0.33	0.63	63.6
20.46	7.30	2.00	97			49.6	0.02	0.94	19.0
40.12	5.56	3.74	93			101.9	0.002	0.958	9.4
80.26	3.47	5.83	73						

COMPOUND: Napnthalene/Filtrasorb-400

STRUCTURE:

FORMULA: $C_{10}H_8$ MOL. WT. 128.19

FREUNDLICH PARAMETERS	pH		
	7.5		
K	176		
1/n	0.524		
Corr. Coef. r	0.993		
INITIAL CONC mg/l	ADSORPTION CAPACITY, mg/gm		
10	588		
1.0	176		
0.1	53		

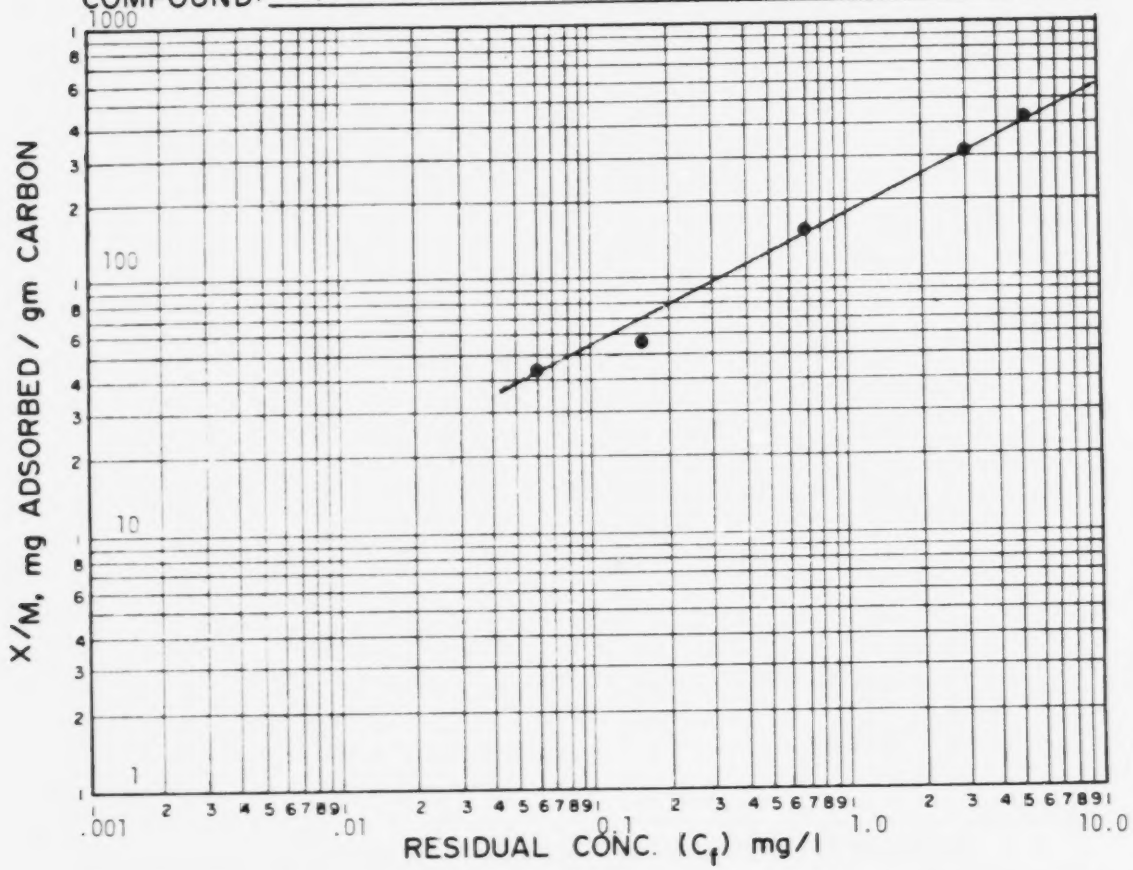
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

Co, mg/l	C_f, mg/l 1.0	0.1	0.01	0.001
10	51	188	634	2121
1.0	--	17	63	212
0.1	--	--	5.7	21
0.01	--	--	--	2

(a) Carbon doses in mg/l at neutral pH

REMARKS:

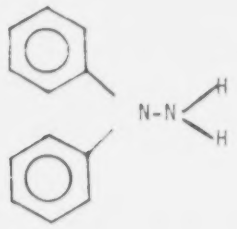
COMPOUND: Naphthalene/Filtrasorb-400



	pH = 7.5			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	9.94	--	--						
11.2	5.3	4.64	414						
22.3	3.0	6.94	311						
56.1	0.71	9.23	165						
168.3	0.17	9.77	58						
224.4	0.06	9.88	44						

COMPOUND: 1,1-Diphenylhydrazine/Darco

STRUCTURE:



FORMULA: $C_{12}H_{12}N_2$ **MOL. WT.** 184.2

FREUNDLICH PARAMETERS	pH		
	7.5		
K	92		
1/n	0.257		
Corr. Coef. r	0.918		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	166		
1.0	92		
0.1	51		

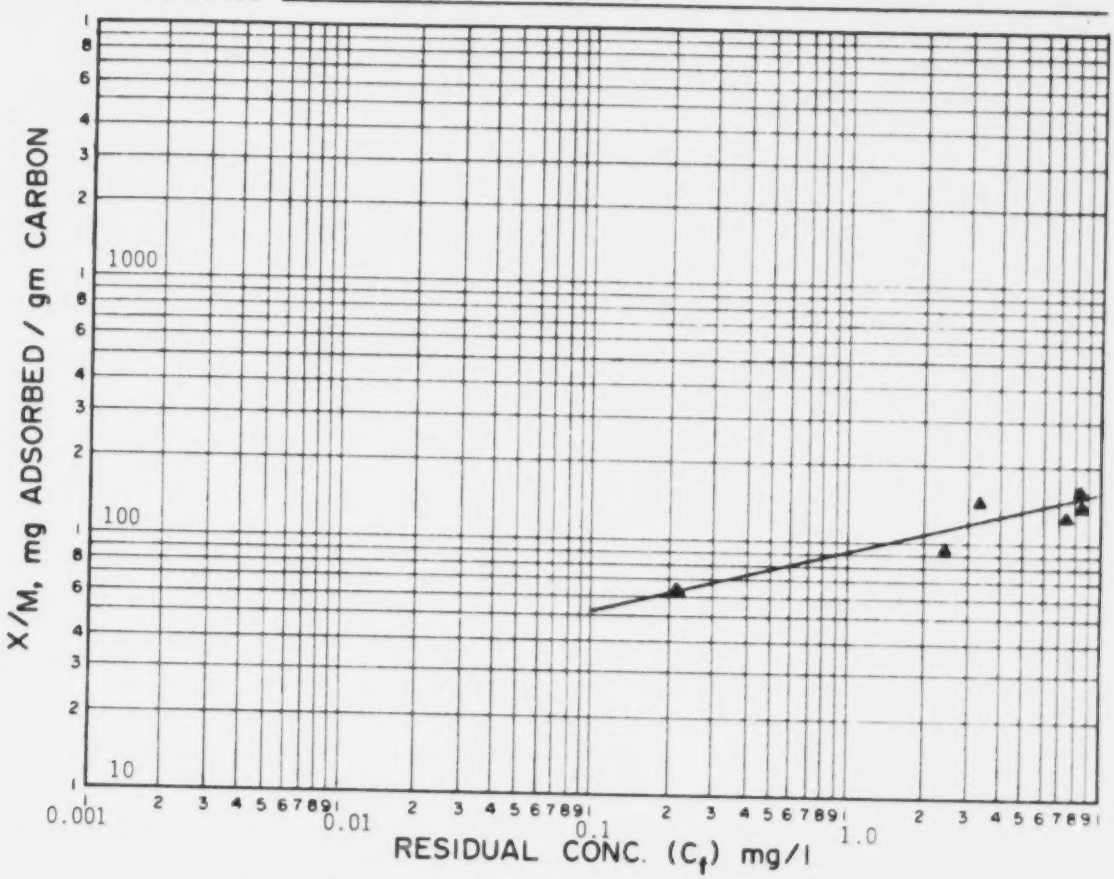
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

	C_f, mg/l			
Co, mg/l	1.0	0.1	0.01	0.001
10	98	194	355	641
1.0	-	19	35	64
0.1	-	-	3	6
0.01	-	-	-	1

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

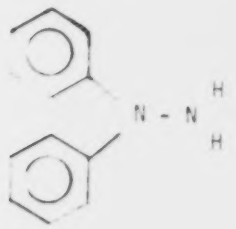
COMPOUND: 1,1-Diphenylhydrazine/Darco



CARBON DOSE mg/l	pH = 7.5			pH =			pH =		
	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	10.03	--	--						
4.04	10.19	--	--						
10.22	8.31	1.72	168						
20.44	7.51	2.88	141						
40.13	3.35	6.68	166						
80.26	2.30	7.73	96						
160.5	0.21	9.02	61						
10.22	8.51	1.52	148						

COMPOUND: 1,1-Diphenylhydrazine/Filtrasorb-400

STRUCTURE:



FORMULA: $C_{12}H_{12}N_2$ MOL. WT. 184.24

FREUNDLICH PARAMETERS	pH		
	7.5		
K	135		
1/n	0.158		
Corr. Coef. r	0.751		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	194		
1.0	135		
0.1	94		

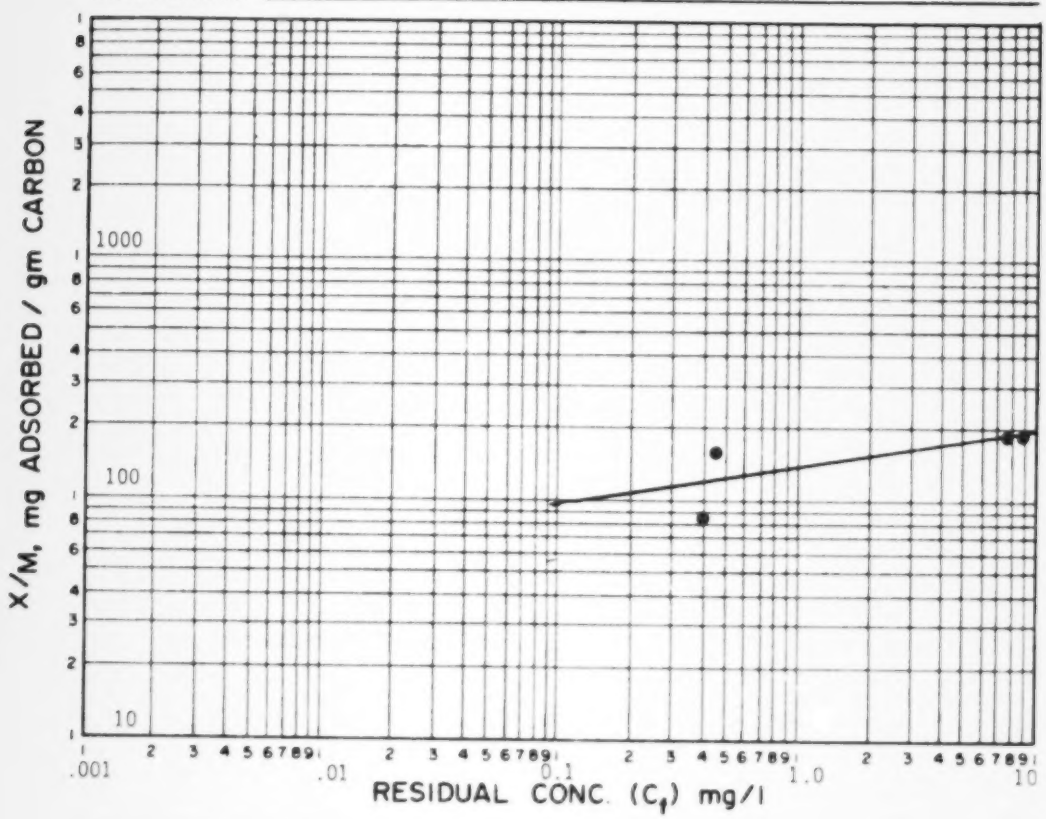
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION(a)

Co, mg/l	C_f, mg/l			
	1.0	0.1	0.01	0.001
10	66	104	153	221
1.0	--	10	15	22
0.1	--	--	1.5	2
0.01	--		--	0.2

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

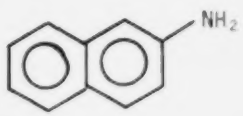
COMPOUND: 1,1-Diphenylhydrazine/Filtrasorb-400



	pH = 7.5			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	9.95								
4.6	9.07	0.88	191						
11.16	7.83	2.12	190						
56.08	0.46	9.49	167						
112.0	0.39	9.56	85						
4.6	9.09	0.86	187						

COMPOUND: β-Naphthylamine/Darco

STRUCTURE:



FORMULA: $C_{10}H_9N$ **MOL. WT.** 143.19

FREUNDLICH PARAMETERS	pH		
	7.5		
K	67		
1/n	0.395		
Corr. Coef. r	0.819		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	171		
1.0	67		
0.1	28		

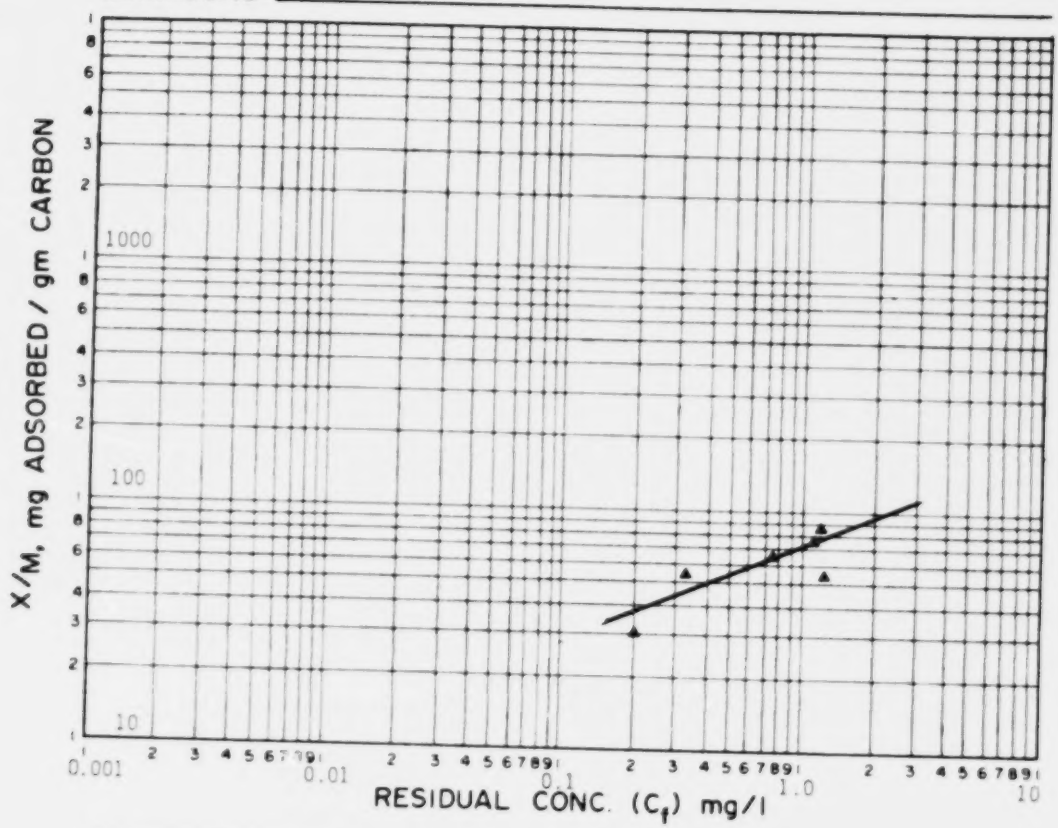
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

Co, mg/l	C_f, mg/l 1.0	0.1	0.01	0.001
10	13	356	892	2219
1.0	--	36	88	222
0.1	--	--	8	20
0.01	--	--	--	2

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

COMPOUND: ·-Naphthylamine/Darco



CARBON DOSE mg/l	pH = 7.5			pH =			pH =		
	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	1.40	--	--						
1.13	1.34	0.06	53						
2.26	1.20	0.20	88						
4.04	1.10	0.30	74						
10.23	0.75	0.65	64						
20.46	0.34	1.06	52						
40.13	0.20	1.20	30						
80.26	0.00	--	--						

COMPOUND: β-Naphthylamine/Filtrasorb-400

STRUCTURE:

FORMULA: $C_{10}H_9N$ MOL. WT. 143.19

FREUNDLICH PARAMETERS	pH		
	7.5		
K	150		
1/n	0.302		
Corr. Coef. r	0.939		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	301		
1.0	150		
0.1	75		

CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

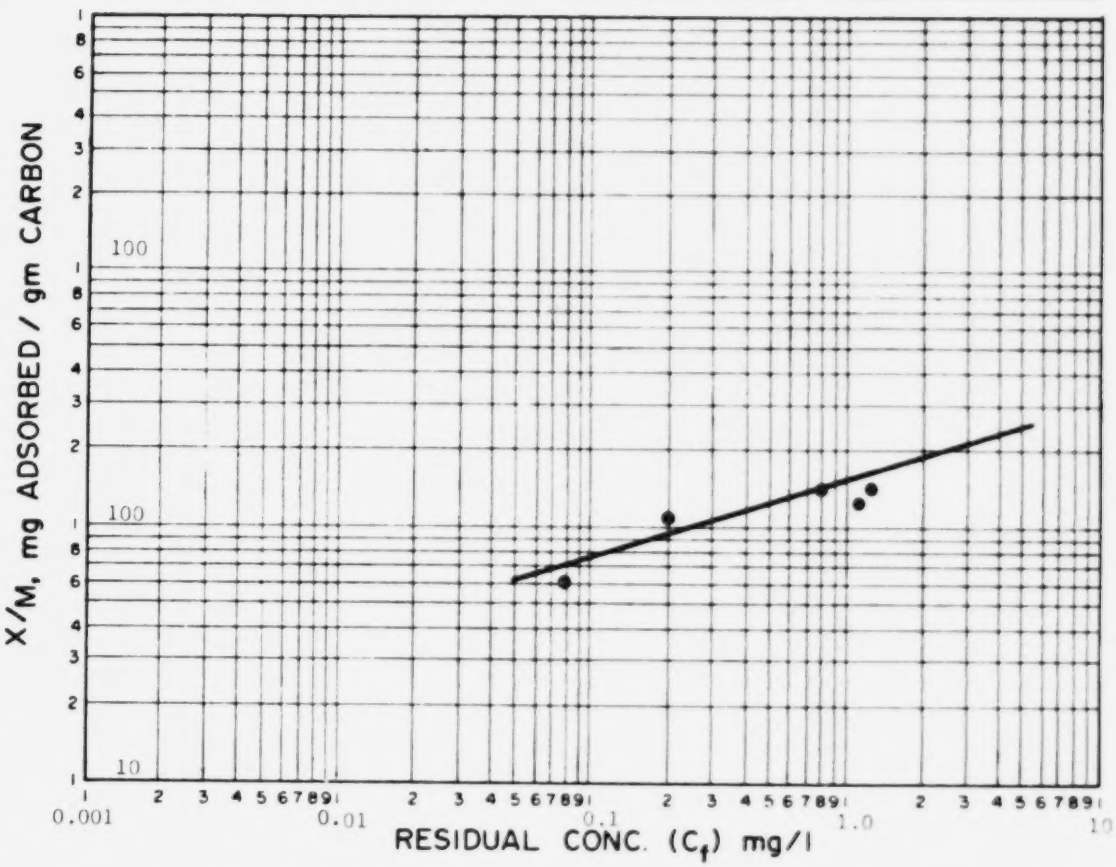
C_f, mg/l

Co, mg/l	1.0	0.1	0.01	0.001
10	120	132	268	536
1.0	-	12	27	54
0.1	-	-	2.4	5.4
0.01	-	-	-	0.5

(a) Carbon doses in mg/l at neutral pH

REMARKS:

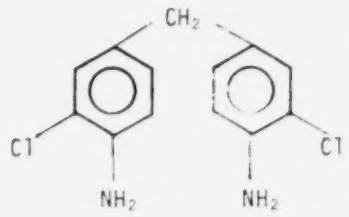
COMPOUND: β-Naphthylamine/Filtrasorb-400



	pH = 7.5			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	1.4	-	-						
1.06	1.24	0.16	151						
2.12	1.10	0.30	142						
4.09	0.78	.62	152						
10.84	0.20	1.20	111						
21.68	0.08	1.32	61						
41.22	0.00	-	-						

COMPOUND: 4,4'-Methylene-Bis(2-chloroaniline)/Darco

STRUCTURE:



FORMULA: $C_{12}H_{12}Cl_2N_2$ **MOL. WT.** 264.28

FREUNDLICH PARAMETERS	pH		
	7.5		
K	93		
1/n	.554		
Corr. Coef. r	.957		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
	333		
	93		
	26		

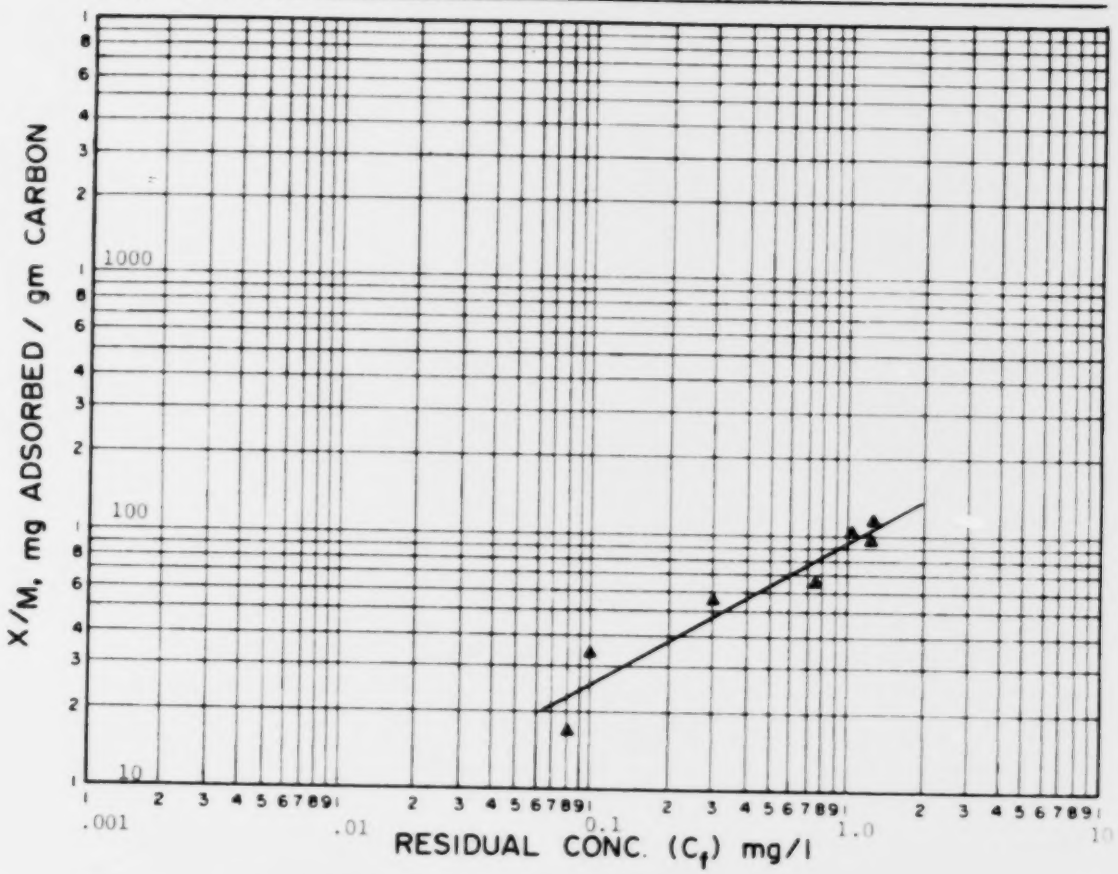
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

	C_f, mg/l			
Co, mg/l	1.0	0.1	0.01	0.001
10	96	381	1377	4937
1.0	-	35	137	443
0.1	-	-	14	44
0.01	-	-	-	4.4

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

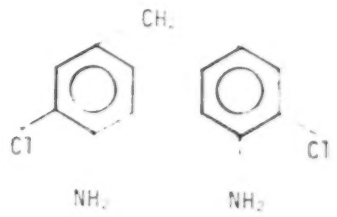
COMPOUND: 4,4'Methylene-Bis(2-chloroaniline)/Darco



CARBON DOSE mg/l	pH = 7.5			pH =			pH =		
	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	1.46	-	-						
1.13	1.33	0.13	115						
2.26	1.24	.22	97						
4.04	1.04	.42	104						
10.23	0.77	.69	67						
20.46	0.30	1.16	57						
40.13	0.10	1.36	34						
80.26	0.08	1.38	17						

COMPOUND: 4,4'-Methylene-Bis(2-chloroaniline)/Filtrasorb-400

STRUCTURE:



FORMULA: $C_{13}H_{12}Cl_2N_2$ **MOL. WT.** 264.28

FREUNDLICH PARAMETERS	pH		
	7.5		
K	188		
1/n	.637		
Corr. Coef. r	.895		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	815		
1.0	188		
0.1	43		

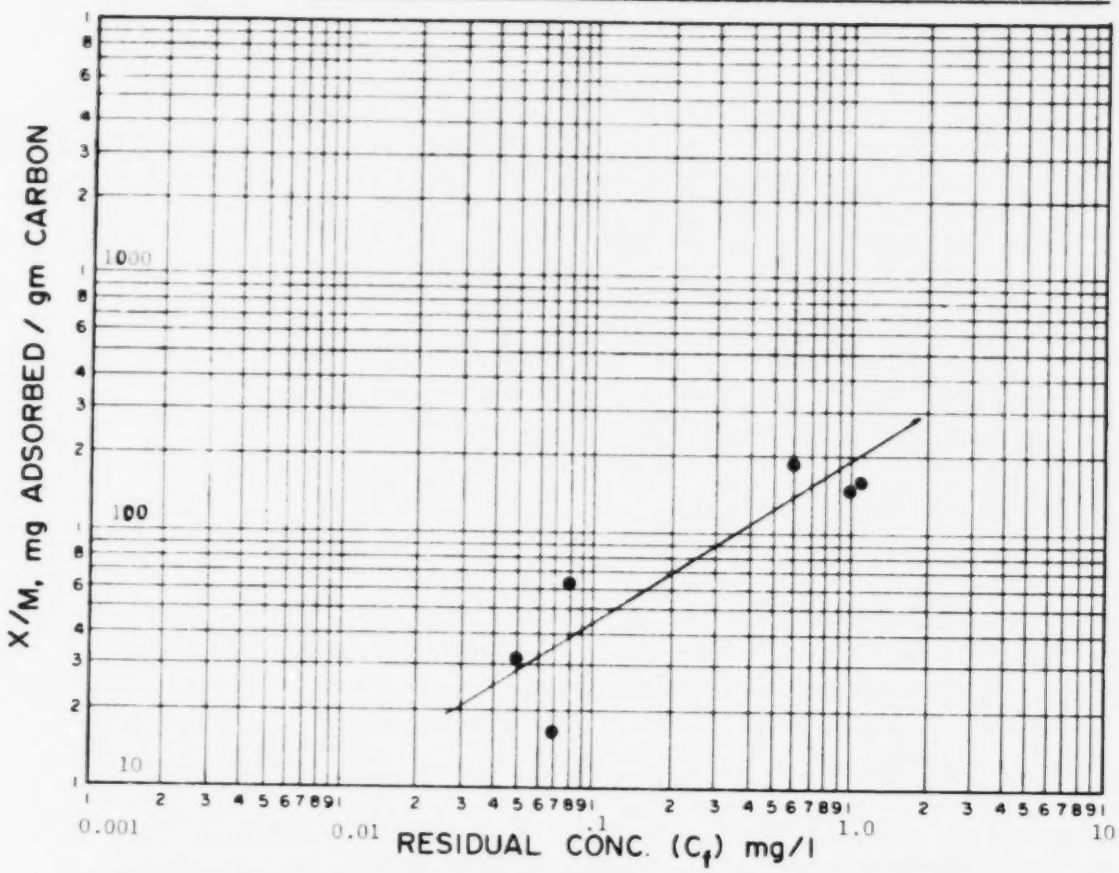
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

	C_f, mg/l			
Co, mg/l	1.0	0.1	0.01	0.001
10	48	228	999	4329
1.0	-	21	99	433
0.1	-	-	9	43
0.01	-	-	-	4

(a) Carbon doses in mg/l at neutral pH

REMARKS:

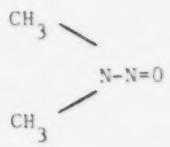
COMPOUND: 4,4'Methylene-Bis(2-chloroaniline)/Filtrasorb-400



	pH = 7.5			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	1.38								
1.13	1.18	0.20	177						
2.26	1.00	.38	168						
4.04	0.60	.78	193						
20.46	0.08	1.30	64						
40.13	0.05	1.33	33						
80.26	0.07	1.31	16						

COMPOUND: N-Dimethyl/nitrosamine/Darco

STRUCTURE:



FORMULA: $(CH_3)_2NNO$ MOL. WT. 74.08

FREUNDLICH PARAMETERS	pH		
	7.5		
K	1.45×10^{-6}		
1/n	8.15		
Corr. Coef. r	.715		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	197		
1.0	1.45×10^{-6}		
0.1	-		

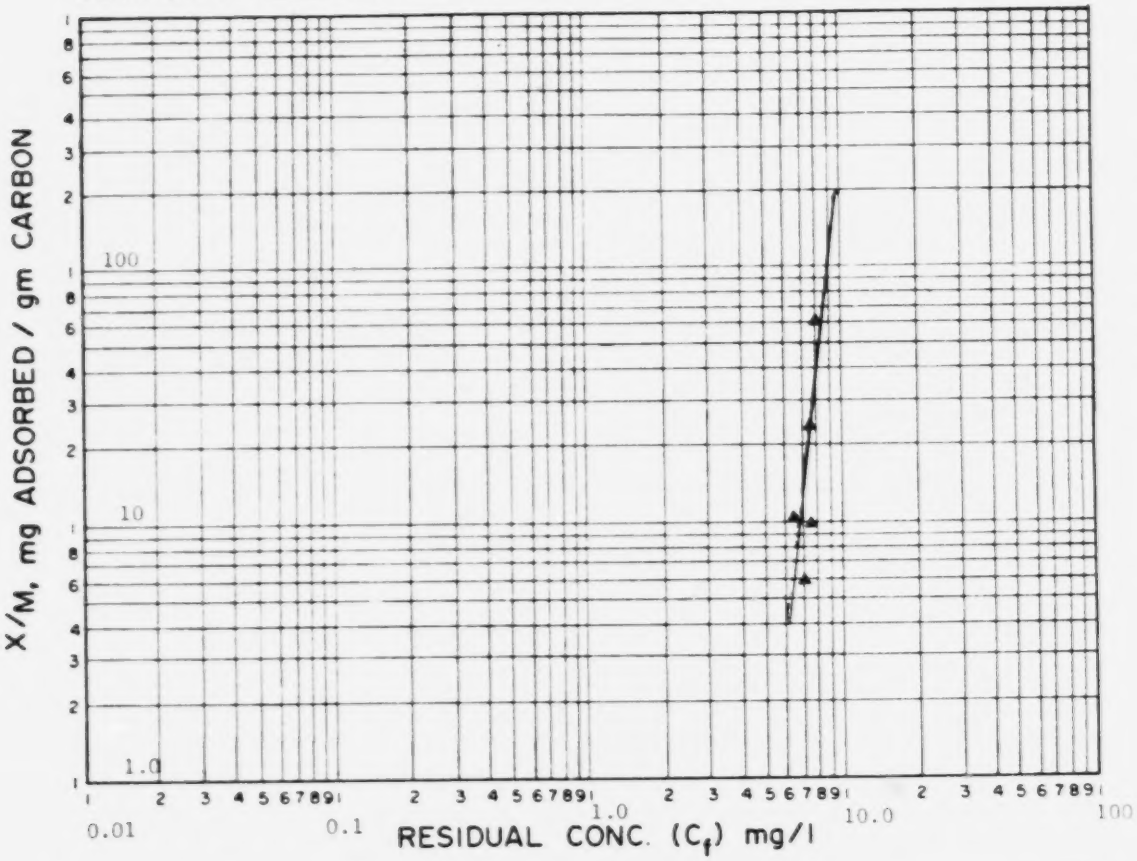
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

	C_f, mg/l			
Co, mg/l	1.0	0.1	0.01	0.001
10	$>10^6$	-	-	-
1.0	-	-	-	-
0.1	-	-	-	-
0.01	-	-	-	-

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

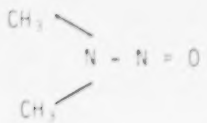
COMPOUND: N-Dimethylnitrosamine/Darco



	pH =			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	8.5	-	-						
4.0	9.5	-	-						
8.1	8.0	0.5	62						
15.3	8.5	-	-						
46.0	7.5	1.0	22						
100.6	7.5	1.0	10						
181.5	6.5	2.0	11						
251	7.0	1.5	6						

COMPOUND: N-Dimethylnitrosamine/Filtrasorb - 400

STRUCTURE:



FORMULA: $(CH_3)_2NNO$ MOL. WT. 74.08

FREUNDLICH PARAMETERS	pH		
	7.5		
K	6.79×10^{-5}		
1/n	6.57		
Corr. Coef. r	0.617		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
10	252		
1.0	6.79×10^{-1}		
0.1			

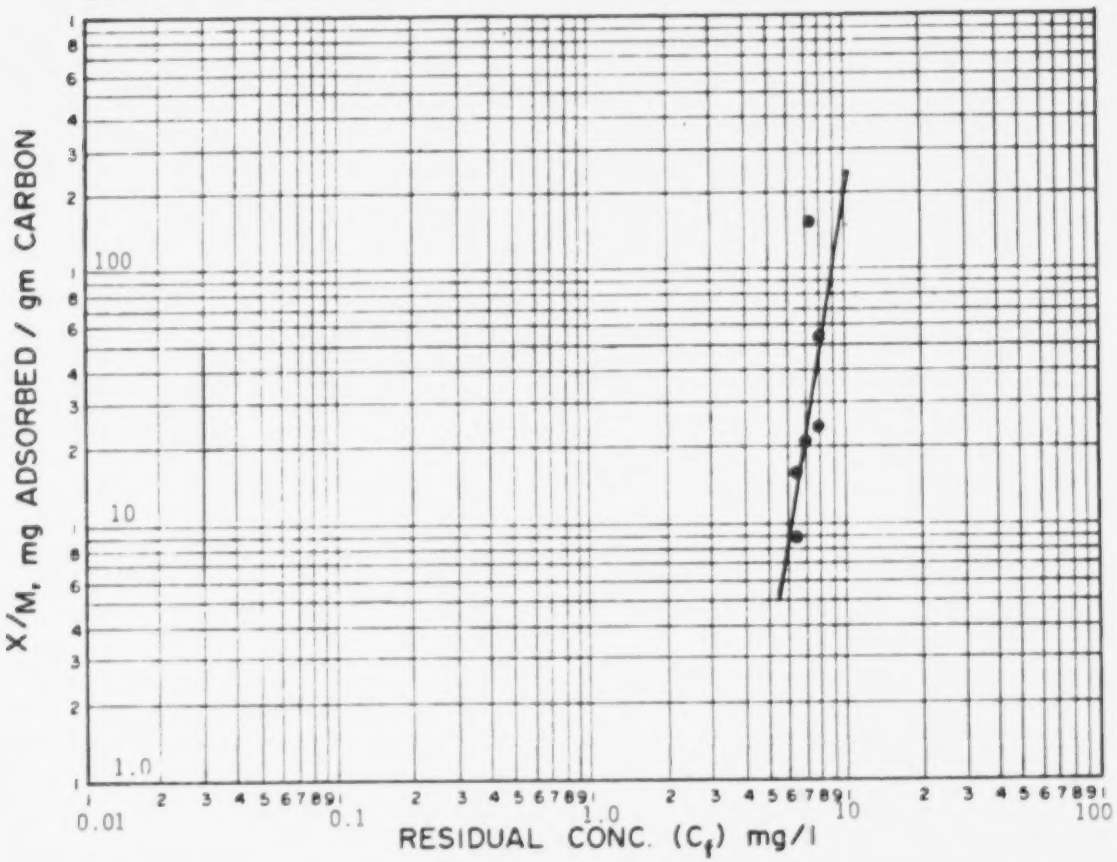
CARBON DOSES REQUIRED TO ACHIEVE INDICATED CHANGE IN CONCENTRATION[a]

	C_f, mg/l			
Co, mg/l	1.0	0.1	0.01	0.001
10	10^{-5}	-	-	-
1.0	-	-	-	-
0.1	-	-	-	-
0.01	-	-	-	-

(a) Carbon doses in mg/l at neutral pH.

REMARKS:

COMPOUND: N-Dimethylnitrosamine/Filtrasorb - 400



	pH = 7.5			pH =			pH =		
CARBON DOSE mg/l	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M	C_f	$C_o - C_f = X$	X/M
0	9.0	--	--						
4.6	9.0	--	--						
9.2	7.5	1.5	163						
18.4	8.0	1.0	54						
41.2	8.0	1.0	24						
96.0	7.0	2.0	21						
146.4	6.5	2.5	17						
288.0	6.5	2.5	9						

APPENDIX B

PREPARATION OF NUTRIENT FOR STATIC AND CONTINUOUS BIODEGRADATION TESTS

NUTRIENT

Reagents

1. Distilled water.

2. Calcium chloride solution:

   Dissolve 27.5 g anhydrous $CaCl_2$ in distilled water and dilute to 1 ℓ.

3. Magnesium sulfate solution:

   Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 ℓ.

4. Ferric chloride solution:

   Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 ℓ. These solutions should be stored in the dark, preferably in a refrigerator, and discarded at the first sign of turbidity.

5. Phosphate buffer solution:

   Dissolve 8.5 g potassium dihydrogen phosphate, KH_2PO_4, 21.75 g dipotassium hydrogen phosphate, K_2HPO_4, 33.4 g disodium hydrogen phosphate heptahydrate, $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g ammonium chloride NH_4Cl, in about 500 ml distilled water and dilute to 1 ℓ.

Preparation of Medium

For each liter of distilled water add 1 ml of each of the following solutions in the order indicated, mixing after each addition:

1. Calcium chloride solution
2. Magnesium sulfate solution
3. Ferric chloride solution
4. Phosphate buffer solution.

Weight 0.055 g of yeast extract (Difco or equivalent), add 1 to 1 ℓ of the above solution and dissolve. Dispense 90 ml of medium into 250-ml Erlenmeyer

flasks. The medium should be used within 3 hours after preparation unless sterilized. If an autoclave is available, larger batches of medium may be prepared, dispensed in flasks, and sterilized at 121°C for 15 min. When this is done, sufficient additional distilled water must be added to the medium to offset the sterilization loss. The flasks should be stoppered with cotton and capped with aluminum foil before sterilization. Foil caps and cotton stoppers are used to retard evaporation and maintain sterility until the medium is used. They are removed during the test.

PREPARATION OF MINERALIZED WATER FOR CARBON ADSORPTION AND OZONATION TESTS

MINERALIZED WATER

Stock Solutions

1. Dissolve 21.96 g potassium dihydrogen phosphate, KH_2PO_4, in 1 ℓ H_2O.

2. Dissolve 128.38 g magnesium sulfate heptahydrate $MgSO_4 \cdot 7H_2O$, in 1 ℓ H_2O.

3. Dissolve 273.7 g calcium chloride hexahydrate $CaCl_2 \cdot 6H_2O$, in 1 ℓ H_2O.

Preparation

Use 95 mℓ of each stock solution in 45 ℓ of water. Adjust the pH from the 6.8 of the stock solution to 7.5 by adding 16.8 g of sodium bicarbonate, $NaHCO_3$.

ANALYSIS OF BENZIDINE PLUS 3,3'-DICHLOROBENZIDINE

A survey of the literature revealed that a number of methods have been reported for the analysis of benzidine in different matrices.[20--25] The procedure of Nony and Bowman[25] was chosen. It involves solvent extraction of the sample with benzene, drying and concentration using a K-D evaporator, derivatization and analysis by gas chromatography-flame ionization detection. The method is described below. The EPA Chloramine T complexation method[26] was not considered because of the possible formation of interferences in the treatment experiments. The procedure of Nony and Bowman was found to be satisfactory. A benzidine recovery of 86.5 percent ± 6.4 percent, was obtained in the analysis of duplicate samples spiked at the ppm level. In several cases, however, the samples were not completely derivatized for some reason. Similar problems were encountered by F. K. Kawahara[26] of EPA's Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, who is also using the Nony and Bowman procedure for the analysis of benzidine in wastewater. Some additional development work will be required before this procedure can be used for routine analysis.